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(54) Aqueous recording liquid, recording method and apparatus using same

(57) An aqueous recording liquid suitable for use in ink jet printing containing a colorant, 2,2,4-trimethyl-1,3-pentanediol, and at least one surfactant selected from polyoxyethylene alkyl ethers and polyoxyethylene alkyl ether acetates.

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Description

[0001] The present invention relates to an aqueous recording liquid suitable either for an on-demand ink jet recording system, such as a piezoelectric system or a thermal system, or for a continuous injection type ink jet recording system such as a charge control system, and more particularly, to an aqueous recording liquid composition which exhibits excellent properties when used for printing on a plain paper and which can be also used as an aqueous recording liquid for a writing utensil, a recorder or a pen plotter.

[0002] In recent years, an ink jet recording system has been rapidly spreading because of its advantages such as compactness, low price, low running cost and low noise. An ink jet printer capable of printing on a non-coated plain paper such as a transfer paper for electrophotography, a printing paper, a typewriter paper, a wire dot printer paper, a word processor paper, a letter paper, a reporting paper is also placed on the market.

[0003] There have been proposed inks for use in such an ink jet printer having improved drying property to obtain an image of higher quality.

[0004] However, it is difficult to obtain an ink satisfying all the requirements; color reproducibility, water resistance, photoresistance, drying property, anti-blurring property and ejection reliability.

[0005] In the case of a color printer, even when no deterioration of image quality is observed in image areas printed in a single color of yellow, magenta or cyan, deterioration of image quality tends to occur in image areas of colors obtained by superimposing two color inks such as red, green and blue. In the case of a printer in which an image is dried without using a fixing unit, when the drying property of an ink is improved by enhancing the penetrability thereof as described in JP-A-S55-29546, the ink has a significant tendency to blur.

[0006] JP-B-S60-23793 suggests that, when dialkyl sulfosuccinate is used as a surfactant of an ink, the drying property of the ink can be improved without deteriorating image quality. However, the pixel diameter of a printed image remarkably varies depending upon the kind of a paper, and the density of the printed images is considerably decreased.

[0007] JP-A-S58-6752 discloses a quick drying ink whose anti-blur property is improved by enhancing the penetrability thereof using a surfactant containing an ethylene oxide having an acetylenic linkage.

[0008] However, some colorants cause the following problems. When an ink containing a direct dye such as DBK 168 is used, the drying rate of the ink cannot be improved due to a hydrophobic interaction between the surfactant and the colorant. When an ink containing a pigment such as carbon black is used, the pigment tends to aggregate, causing clogging of nozzles or inclination of ink ejection direction.

[0009] For the purpose of improving drying rate, JP-A-H8-113739 discloses an ink containing a dye and water-soluble glycol ethers and JP-A-H10-95941 proposes an ink composition composed of a pigment, glycol ethers such as diethyleneglycol mono-n-butyl ether and water.

[0010] However, a large amount of glycol ethers must be added to improve the drying rate of the ink, which is not preferable from the viewpoint of odor and safety.

[0011] JP-A-S56-57862 discloses an ink containing a strong basic substance. With this ink, an image with no deterioration can be formed on an acidic paper sized with rosin. However, this ink is not suitable for a paper prepared using alkyl ketene dimer or alkenyl sulfosuccinic acid as a sizing agent. Even on an acidic paper, image deterioration is observed in image areas of colors obtained by superimposing two colors.

[0012] JP-A-138374 discloses an aqueous recording ink comprising a water-soluble dye, water and a benzyl ether having a specific structure. It is also suggested therein adding to the ink a vegetable oil, an unsaturated fatty acid, a higher alcohol, a fatty acid ester, an oily substance such as a mineral oil, and a hardly or slightly water-soluble solvent having a hydroxyl group in the molecular such as 2-ethyl-1,6-hexanediol, diethylene glycol hexyl ether, ethylene oxide adduct of acetylene glycol (having addition mole number of not greater than 5) and ethylene glycol benzyl ether for the purpose of further improving the penetrability of the ink. However, these inks have a problem in safety. Moreover, these inks have a significant problem in stability. The oily substance, the hardly or slightly water-soluble solvent benzyl ether and so on are separated at a certain environmental temperature.

[0013] Japanese Patent No. 2894568 proposes an ink jet ink comprising a composition containing a colorant and a liquid medium containing at least 60 % by weight of water and 0.2 to 30 % by weight of an alkylene glycol having 7 to 10 carbon atoms. Compounds shown as preferred examples of the alkylene glycol having 7 to 10 carbon atoms are 1,7-heptanediol, 2,6-heptanediol, 2,4-dimethyl-2,4-pentanediol, 3-ethyl-1,3-pentanediol and so on. It is said that, by addition of the compounds, there can be provided an ink which has "improved anti-blurring property, drying property and penetrability for a plain paper",
which has "good balance between blurring property and penetrability" and which is "highly reliable in preventing clogging of ejection nozzle". In reality, however, the penetrability of the ink cannot sufficiently improved by addition of the above compounds and thus the drying property of the ink is still poor. Also, the ink is apt to blur on some types of papers. Namely, none of the problems of prior arts is not overcome.

[0014] Japanese Patent No. 2714482 proposes an ink jet ink containing an aliphatic diol compound having at least 6 carbon atoms and having a water solubility of at least 4.5 % by weight at 25°C. The diol compounds shown as the

examples include 2-ethyl-2-methyl-1,3-propanediol, 3,3-dimethyl-1,2-butanediol, 2,2-diethyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2,4-dimethyl-2,4-pentanediol, 2,5-dimethyl-2,5-hexanediol, 5-hexene-1,2-diol, and so on. However, any inks containing the above compound cannot have sufficient penetrability and causes color bleeding or feathering.

[0015] JP-A-H6-157959 proposes an aqueous ink to which 2-ethyl-1,3-hexanediol is added for the purpose of improving permeability, and a recording method using the same.

[0016] 2-Ethyl-1,3-hexanediol is not included in the examples of the usable compounds shown in Japanese Patent No. 2894568 but has been found to be able to be provide an aqueous ink composition which can satisfy the properties required of an ink jet ink, which is excellent in penetrability and drying property, and which can overcome the problem of image deterioration, and which can provide a recording method for producing a high-quality image using the ink composition. Since 2-ethyl-1,3-hexanediol can impart high ejection stability on high-frequency driving to an ink with a small amount, the method of recording using the ink is high in safety.

[0017] However, with the rapid progress of technologies in recent years, the printing speed of an ink jet printer has been greatly increased and it is not unthinkable that it will be much faster in the future. Under such circumstances, the ink is required to cause no color bleeding in printing at a higher speed and to dry quickly without transferring to a finger even if rubbed therewith immediately after printing.

[0018] In general, a quick drying ink has high penetrability. At the same time, a colorant in the ink is penetrated into a paper in the thickness direction thereof so largely that the image density tends to be decreased and strike-through is likely to occur. It is apparent that double-side printing will be essential with the progress of an ink jet printer and for the purpose of reducing paper consumption as an environmental issue. Thus, an aqueous ink having high drying property and causing so little strike-through as to permit double-side printing is demanded.

[0019] As has been described above, an aqueous ink jet ink which satisfies various requirements as an ink jet ink, which has high penetrability and drying property irrespective of the type of a colorant or the type of a paper, and which is capable of producing a high quality image with little strike-through is still required to be developed.

[0020] In recent years, a system for reading out recorded information printed with an ink which is invisible under ordinary circumstances with infrared rays or ultraviolet rays has been put to practical use in the fields of bar code printing and post mark printing. In view of preventing environmental pollution, application of an aqueous type recording liquid to such a system is under consideration. Additionally, in order to cope with such a system where high-speed processing is essential, an aqueous recording liquid having high penetrability is demanded.

[0021] The present invention has been made in view of the above problems.

[0022] In accordance with the present invention, there is provided an aqueous recording liquid comprising a colorant, 2,2,4-trimethyl-1,3-pentanediol, and at least one surfactant selected from the group consisting of polyoxyethylene alkyl ethers and polyoxyethylene alkyl ether acetates.

[0023] In another aspect, the present invention provides a recording method for forming an image on a recording medium, comprising ejecting the above aqueous recording liquid as droplets onto said recording medium from a minute ejection nozzle.

[0024] The present invention further provides a recording liquid cartridge having a recording liquid container containing the above aqueous recording liquid.

[0025] The present invention further provides an ink jet recording device comprising the above recording liquid cartridge.

[0026] The present invention will now be described in detail below with reference to the accompanying drawings, in which:

FIG. 1 is a schematic front view illustrating an embodiment of an ink jet recording apparatus mounting an ink cartridge containing an aqueous recording liquid to which the present invention is applied;

FIG. 2 is a perspective view of an external appearance of the ink cartridge before lorded in the recording apparatus of FIG. 1;

FIG. 3 is a front cross-sectional view of the ink cartridge of FIG. 2; and

FIG. 4 is a perspective view of an external appearance of the recording unit integrated with a recording head.

[0027] The aqueous recording liquid according to the present invention comprises at least a colorant, 2,2,4-trimethyl-1,3-pentanediol, and a polyoxyethylene alkyl ether surfactant and/or a polyoxyethylene alkyl ether acetate surfactant.

[0028] The polyoxyethylene alkyl ether is preferably an ether represented by the general formula (1):

$$R_1O(CH_2CH_2O)_pH \qquad (1)$$

wherein R_1 represents a straight or branched alkyl group having 8 to 14 carbon atoms and p represents an integer of 1 to 30.

[0029] The polyoxyethylene alkyl ether acetate surfactant is preferably an acetate represented by the general formula (2) :

$$R_2O(CH_2CH_2O)_qCH_2COOM \quad (2)$$

wherein R_2 represents a straight or branched alkyl group having 8 to 14 carbon atoms, q represents an integer of 3 to 8, and M represents an alkali metal ion, a quaternary ammonium, a quaternary phosphonium or an alkanolamine.

[0030] The aqueous recording liquid according to the present invention has excellent storage stability, and exhibits high wettability on a paper surface and a high rate of penetration into a paper irrespective of the type of the paper. Additionally, the aqueous recording liquid is much less liable to cause image deterioration as compared with a conventionally known recording liquid whose penetrability is enhanced. When used in an ink jet recording system, the aqueous recording liquid exhibits high ejection properties without causing clogging of nozzles. Moreover, the aqueous recording liquid can exhibit such excellent properties in combination with various colorants.

[0031] Examples of compounds represented by the formula (1) include compounds represented by the following formulas (1-1) to (1-13) but the present invention is not limited thereto.

$$C_8H_{17}O(C_2H_4O)_2H \quad (1\text{-}1)$$

$$C_{10}H_{21}O(C_2H_4O)_4H \quad (1\text{-}2)$$

$$C_{12}H_{25}O(C_2H_4O)_3H \quad (1\text{-}3)$$

$$C_{12}H_{25}O(C_2H_4O)_7H \quad (1\text{-}4)$$

$$C_{12}H_{25}O(C_2H_4O)_{12}H \quad (1\text{-}5)$$

$$C_{13}H_{27}O(C_2H_4O)_3H \quad (1\text{-}6)$$

$$C_{13}H_{27}O(C_2H_4O)_5H \quad (1\text{-}7)$$

$$C_{13}H_{27}O(C_2H_4O)_7H \quad (1\text{-}8)$$

$$C_{13}H_{27}O(C_2H_4O)_9H \quad (1\text{-}9)$$

$$C_{13}H_{27}O(C_2H_4O)_{12}H \quad (1\text{-}10)$$

$$C_{13}H_{27}O(C_2H_4O)_{20}H \quad (1\text{-}11)$$

$$C_{13}H_{27}O(C_2H_4O)_{30}H \quad (1\text{-}12)$$

$$C_{14}H_{29}O(C_2H_4O)_{30}H \quad (1\text{-}13)$$

[0032] These compounds may be used alone or in combination. A compound which is not easily dissolved in the recording liquid when used alone is solubilized when mixed with other compound and can be stably present therein.

[0033] Examples of commercially available surfactants containing such a compound as the main component include BT series available from Nikko Chemicals Co., Ltd., Softanol series available from Nippon Shokubai Co., Ltd., and Dispanol available from Nippon Oils & Fats Co., Ltd. These are preferably employed for the purpose of the present invention.

[0034] Examples of compounds represented by the general formula (2) include compounds represented by the formulas (2-1) to (2-13) in which M is as defined above, but the present invention is not limited thereto.

$$C_8H_{17}O(C_2H_4O)_3CH_2COOM \quad (2\text{-}1)$$

$$C_{10}H_{21}O(C_2H_4O)_4CH_2COOM \quad (2\text{-}2)$$

$$C_{12}H_{25}O(C_2H_4O)_3CH_2COOM \quad (2\text{-}3)$$

$$C_{12}H_{25}O(C_2H_4O)_4CH_2COOM \quad (2\text{-}4)$$

$$C_{12}H_{25}O(C_2H_4O)_5CH_2COOM \quad (2\text{-}5)$$

$$C_{12}H_{25}O(C_2H_4O)_{12}CH_2COOM \quad (2\text{-}6)$$

$$C_{13}H_{27}O(C_2H_4O)_3CH_2COOM \quad (2\text{-}7)$$

$$C_{13}H_{27}O(C_2H_4O)_5CH_2COOM \quad (2\text{-}8)$$

$$C_{13}H_{27}O(C_2H_4O)_7CH_2COOM \quad (2\text{-}9)$$

$$C_{13}H_{27}O(C_2H_4O)_9CH_2COOM \quad (2\text{-}10)$$

$$C_{13}H_{27}O(C_2H_4O)_{12}CH_2COOM \quad (2\text{-}11)$$

$$C_{14}H_{29}O(C_2H_4O)_3CH_2COOM \quad (2\text{-}12)$$

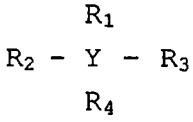
$$C_{14}H_{29}O(C_2H_4O)_{12}CH_2COOM \quad (2\text{-}13)$$

[0035] These compounds may be used alone or in combination. A compound which is not easily dissolved in the recording liquid when used alone is solubilized when mixed with other compound and can be stably present therein. It is preferred that inorganic salts produced as byproducts at the time of synthesis of the compound be removed with an ion-exchange resin.

[0036] Examples of commercially available surfactants containing such a compound as the main component include

NIKKOLECT series and NIKKOLAKYPO series available from Nippon Chemicals Co., Ltd. Other surfactants such as Beaulight series available from Sanyo Chemical Industries, Ltd. can be also employed.

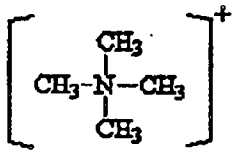
[0037] The polyoxyethylene alkyl ether acetate surfactant is used in the form of a salt with M. As the counter ion M, an alkali metal ion, quaternary ammonium, quaternary phosphonium, or alkanolamine is preferably employed. Also, when a sodium cation, a lithium cation, and/or a cation of quaternary ammonium, quaternary phosphonium or alkanolamine reperesented by the general formula (4) is used as the counter ion M, the dissolution stability is further enhanced.



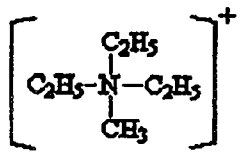
(4)

wherein Y represents a nitrogen atom or a phosphorus atom, R_1 to R_4 each represent a hydrogen atom, an alkyl group, a hydroxyalkyl group, and an alkyl group halide, respectively. The "alkyl" is preferably a lower alkyl preferably having 1 to 4 carbon atoms.

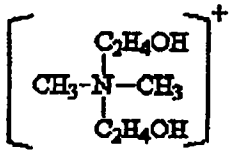
[0038] The polyoxyethylene alkyl ether acetate surfactant in the form of a salt may be prepared by, for example, adding a hydroxide to the corresponding acid. For example, a surfactant in the form of a lithium salt may be prepared by adding lithium hydroxide to polyoxyethylene alkyl ether acetatic acid. When the surfactant is a salt with quaternary ammonium, quaternary phosphonium or alkanolamine represented by the general formula (4), the surfactant is prepared by adding one of the following hydroxides to polyoxyethylene alkyl ether acetatic acid.



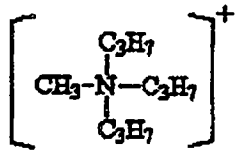
OH^- (13-1)



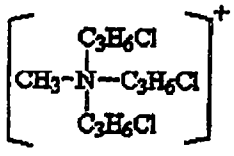
OH^- (13-2)



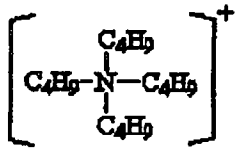
OH^- (13-3)



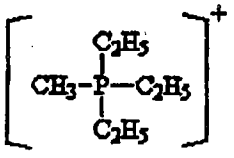
OH^- (13-4)



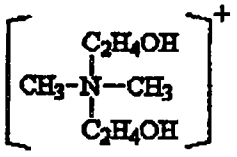
OH^- (13-5)



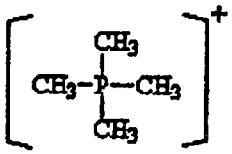
OH^- (13-6)



OH^- (13-7)



OH^- (13-8)



(13-9)

$(C_2H_4OH)_3NH^+ \ OH^-$ (13-10)

[0039] The polyoxyethylene alkyl ether surfactant and polyoxyethylene alkyl ether acetate surfactant may be used alone or in combination.

[0040] According to the present invention, there can be obtained a recording liquid which has significantly high penetrability, which is stable without having separation therein and which has high safety by using 2,2,4-trimethyl-1,3-pentanediol together with the polyoxyethylene alkyl ether surfactant and/or polyoxyethylene alkyl ether acetate surfactant.

[0041] While not wishing to be bound by the theory, the mechanism by which the above functions are attained by the use of the polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant in conjunction with 2,2,4-trimethyl-1,3-pentanediol is assumed to be as follows.

[0042] 2,2,4-Trimethyl-1,3-pentanediol which has an asymmetric molecular structure having a branch easily adsorbs onto a surface of a colorant in a recording liquid mainly composed of water. Also, 2,2,4-trimethyl-1,3-pentanediol, which has a relatively small molecular weight as compared with the surfactant, adsorbs onto a surface of the colorant at a high adsorption rate. Namely, when 2,2,4-trimethyl-1,3-pentanediol adsorbs to the surface of the colorant, the surface tension of the recording liquid is rapidly decreased as if a surfactant is added thereto.

[0043] However, 2,2,4-trimethyl-1,3-pentanediol has a small difference between hydrophilicity and hydrophobicity as compared with a surfactant, a large amount of 2,2,4-trimethyl-1,3-pentanediol must be added to obtain high penetrability with 2,2,4-trimethyl-1,3-pentanediol alone. A recording liquid containing a large amount of 2,2,4-trimethyl-1,3-pentanediol is not preferable because it has problems of low safety, phase separation, adsorption to a colorant, aggregation and so on.

[0044] It is also known that a polyoxyethylene alkyl ether surfactant and a polyoxyethylene alkyl ether acetate reduce surface tension and improve penetrability. However, since the surfactants do not necessarily have a high adsorption rate because of the size and shape of the molecules thereof, it is impossible to obtain sufficient penetrability therewith.

[0045] The present inventors have found that when 2,2,4-trimethyl-1,3-pentanediol is used together with polyoxyethylene alkyl ether surfactant and/or polyoxyethylene alkyl ether acetate surfactant, a significantly high penetration properties can be obtained by a synergistic effect with a small amount of addition, and has accomplish the present invention. There is also obtain an advantage that 2,2,4-trimethyl-1,3-pentanediol is an industrially advantageous material and treated in relatively in a large amount so that the recording liquid can be produced at a relatively low cost.

[0046] Description will be made of the amount to be added in the recording liquid.

[0047] The polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant is preferably added in an amount of not less than 0.01 % by weight and not greater than 4 % by weight based on the total amount of the recording liquid.

[0048] When the amount of polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant is less than 0.01 % by weight, the penetrability of the recording liquid cannot be sufficiently improved. When the amount is greater than 4 % by weight, the polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant is not stably dissolved in the recording liquid or increases the viscosity of the recording liquid even if dissolved therein, causing problems in storage stability and ejection stability in an ink jet system.

[0049] The polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant is more preferably added in an amount of not less than 0.05 % by weight and not greater than 2 % by weight.

[0050] 2,2,4-Trimethyl-1,3-pentanediol is preferably added in an amount of not less than 0.1 % by weight and not greater than 8 % by weight based on the total amount of the recording liquid.

[0051] When the amount of 2,2,4-trimethyl-1,3-pentanediol is less than 0.1 % by weight, the penetrability of the recording liquid is not sufficiently improved. When the amount is greater than 8 % by weight, 2,2,4-trimethyl-1,3-pentanediol is not stably dissolved in the recording liquid, causing problems in storage stability and ejection stability in an ink jet system. 2,2,4-Trimethyl-1,3-pentanediol is more preferably added in an amount of not less than 0.5 % by weight and not grater than 5 % by weight.

[0052] 2,2,4-Trimethyl-1,3-pentanediol has a low solubility in water and thus is easily separated under certain environmental conditions when added alone in a recording liquid. However, when 2,2,4-trimethyl-1,3-pentanediol is added in combination with the polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant, these are compatibilized with each other, whereby a stable recording liquid can be obtained.

[0053] When 2,2,4-trimethyl-1,3-pentanediol is mixed with the polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant, a higher penetrability of the recording liquid can be obtained in addition to

the stability by a synergistic effect thereof with a smaller amount thereof as compared with a recording liquid in which 2,2,4-trimethyl-1,3-pentanediol or the surfactant is added alone. Also, the recording liquid has less solvent odor and higher safety as compared with a conventional recording liquid whose permeability is enhanced by adding a large amount of ethers of polyhydric alcohols.

[0054] Japanese Patent No. 2894568 proposes an ink jet ink comprising a composition containing water and a liquid medium containing not less than 60 % by weight of water and 0.2 to 30 % by weight of an alkylene glycol having 7 to 10 carbon atoms. It is, however, apparent that the bonding position of the hydroxyl group and the number of carbon atoms in the compound make a large difference in its hydrophilicity and the penetrability of an ink containing the compound.

[0055] 2,2,4-Trimethyl-1,3-pentanediol according to the present invention is not shown as an example of usable compounds in Japanese Patent No. 2894568 but has been found among various compounds by the present inventors as a result of zealous studies. It is obvious that a recording liquid according to the present invention, in which 2,2,4-trimethyl-1,3-pentanediol is used in combination with the polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant, can have higher penetrability and anti-blur property than a recording liquid according to Japanese Patent No. 2894568, which merely refers that an alkylene glycol having 7 to 10 carbon atoms is effective.

[0056] In a bubble jet or thermal recording method in which recording is conducted by applying thermal energy to an ink and ejecting the ink as droplets from a minute pore, 2-propanol is conventionally added to a recording liquid to obtain ejection stability. When 2,2,4-trimethyl-1,3-pentanediol is added in place of 2-propanol, the wettability of the recording liquid to a thermal element is improved and high ejection stability and frequency stability can be obtained with a small amount of addition. Additionally, a problem concerning safety caused by use of 2-propanol is also solved.

[0057] The present inventors have also found that when 2-pyrolydone is added in a recording liquid, there can be obtained good effects of improving image density and preventing strike-through. This is thought to be because the recording liquid containing 2-pyrolydone wets and spreads well on a surface of a paper and is relatively restrained from penetrating into the paper in the thickness direction thereof so that the colorant tends to remain in a region adjacent the surface of the paper. 2-Pyrolydone is preferably added in an amount of 0.05 to 8 % by weight, more preferably 0.5 to 4 % by weight.

[0058] The present inventors have also found that, when a wetting agent is added to the recording liquid according to the present invention in an amount of 5 to 50 % by weight for the purpose of preventing clogging of ejection nozzle caused by drying of the recording liquid and improving dissolution stability, clogging of an ejection port of an ink jet head hardly occurs and normal printing can be performed even when water in the recording liquid is evaporated. Even when clogging occurs, the ink jet head can be restored to normal printing conditions with a simple cleaning operation. As the wetting agent, a low-volatile water-soluble organic solvent is preferred.

[0059] The low volatile water-soluble organic solvent also serves as dissolution aid for the polyoxyethylene alkyl ether surfactant and/or the polyoxyethylene alkyl ether acetate surfactant (which will be hereinafter referred to as component (B)) and 2,2,4-trimethyl-1,3-pentanediol (which will be hereinafter referred to as component (A)) and thus can further improve the storage stability and ejection stability of the recording liquid.

[0060] Examples of the low-volatile water-soluble organic solvent include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polyethylene glycol, polypropylene glycol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2-methyl-2,4-pentanediol, 1,6-hexanediol, glycerin, 1,2,6-hexanetriol, 1,2,4-butanetriol, 1,2,3-butanetriol, and petriol;

polyhydric alcohol alkyl ethers such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, tetraethylene glycol monomethyl ether, and propylene glycol monoethyl ether;

polyhydric alcohol aryl ethers such as ethylene glycol monophenyl ether, and ethylene glycol monobenzyl ether;

a nitrogen-containing heterocycle compound such as 2-pyrolidone, N-methyl-2-pyrolidone, N-hydroxyethyl-2-pyrolidone, 1,3-dimethylimidazolidinone, ε-caprolactam, and γ-butyrolactone;

amides such as formamide, N-methylformamide and N,N-dimethylformamide;

amines such as monoethanolamine, diethanolamine, triethanolamine, monoethylamine, diethylamine and triethylamine;

a sulfur-containing compound such as dimethyl sulfoxide, sulfolane, thiodiethanol, thiodiglycol;

propylene carbonate; and ethylene carbonate.

[0061] The solvents are used alone or in combination, as a mixture with water.

[0062] For a reason of compatibility with the components (A) and (B), glycerin, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, 1,5-pentanediol, tetraethylene glycol, 1,6-hexanediol, 2-methyl-2,4-pentanediol, polyethylene glycol, 1,2,4-butanetriol, 1,2,6-hexanetriol, thiodiglycol, 2-pyrolidone, N-methyl-2-pyrolidone, N-hydroxyethyl-2-pyrolidone, or 1,3-dimethyl-2-imidazolidinone is preferred. For reasons of safety and price, glycerin or diethylene glycol, or a mixture thereof

is especially preferred.

[0063] The low-volatile water-soluble organic solvent is preferably added to the recording liquid composition in an amount of not less than 5 % by weight and not more than 50 % by weight, more preferably not less than 8 % by weight and not more than 30 % by weight. When the amount of the low-volatile water-soluble organic solvent is less than 5 % by weight, a sufficient effect of preventing water in the recording liquid from evaporating can not be obtained. Also, the effect as the dissolution aid may be insufficient and the storage stability and ejection stability of the recording liquid may be impaired, although it depends upon the contents of polyoxyethylene alkyl ether surfactant, polyoxyethylene alkyl ether acetate surfactant and 2,2,4-trimethyl-1,3-pentanediol. When the amount is over 50 % by weight, the ejection stability of the recording liquid is lowered due to an increase in the viscosity thereof, or terrible cockling is apt to occur at printed image portions, as compared with the case where the content of the solvent is in the above range.

[0064] In order to obtain a high quality image by an ink jet recording method, adjustment of wettability of the recording liquid to a part constituting an ink jet head is an important factor. Thus, a surfactant may be additionally added to the recording liquid of the present invention for the purpose of adjusting the wettability thereof.

[0065] Examples of the surfactant include an anionic surfactant such as an ammonium salt of polyoxyethylene alkyl ether sulfate; a cationic surfactant such as quaternary ammonium salts; an ampholytic surfactant such as imidazoline derivatives; a nonionic surfactant such as polyoxyethylene alkyl phenyl ether, polyoxyethylene alkyl ester, polyoxyethylene alkylamine, polyoxyethylene alkylamide, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, ethylene oxide adducts of acetylene alcohol; and a fluorochemical surfactant.

[0066] The surfactant is preferably added in such an amount that adjusts the recording liquid to desired physical properties.

[0067] The colorant used in the present invention comprises a pigment and/or a dye.

[0068] As a water-soluble dye used as the colorant, dyes classified in color index into acid dyes, direct dyes, basic dyes, reactive dyes, and food dyes are employed. These dyes may be used alone or in combination, or may be mixed with other colorant such as a pigment when desired. The colorants may be added in such an amount that does not deteriorate the effect of the present invention.

[0069] Specific examples of acid dyes and food dyes include

C.I. Acid Yellow 17, 23, 42, 44, 79, 142;
C.I. Acid Red 1, 8, 13, 14, 18, 26, 27, 35, 37, 42, 52, 82, 87, 89, 92, 97, 106, 111, 114, 115, 134, 186, 249, 254, 289;
C.I. Acid Blue 9, 29, 45, 92, 249;
C.I. Acid Black 1, 2, 7, 24, 26, 94;
C.I. Food Yellow 2, 3, 4;
C.I. Food Red 7, 9, 14; and
C.I. Food Black 1, 2.

[0070] Specific examples of direct dyes include

C.I. Direct Yellow 1, 12, 24, 26, 33, 44, 50, 120, 132, 142, 144, 86;
C.I. Direct Red 1, 4, 9, 13, 17, 20, 28, 31, 39, 80, 81, 83, 89, 225, 227;
C.I. Direct Orange 26, 29, 62, 102;
C.I. Direct Blue 1, 2, 6, 15, 22, 25, 71, 76, 79, 86, 87, 90, 98, 163, 165, 199, 202; and
C.I. Direct Black 19, 22, 32, 38, 51, 56, 71, 74, 75, 77, 154, 168, 171.

[0071] Specific examples of basic dyes include

C.I. Basic Yellow 1, 2, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 40, 41, 45, 49, 51, 53, 63, 65, 67, 70, 73, 77, 87, 91;
C.I. Basic Red 2, 12, 13, 14, 15, 18, 22, 23, 24, 27, 29, 35, 36, 38, 39, 46, 49, 51, 52, 54, 59, 68, 69, 70, 73, 78, 82, 102, 104, 109, 112;
C.I. Basic Blue 1, 3, 5, 7, 9, 21, 22, 26, 35, 41, 45, 47, 54, 62, 65, 66, 67, 69, 75, 77, 78, 89, 92, 93, 105, 117, 120, 122, 124, 129, 137, 141, 147, 155; and
C.I. Basic Black 2, 8.

[0072] Specific examples of reactive dyes include

C.I. Reactive Black 3, 4, 7, 11, 12, 17;
C.I. Reactive Yellow 1, 5, 11, 13, 14, 20, 21, 22, 25, 40, 47, 51, 55, 65, 67;
C.I. Reactive Red 1, 14, 17, 25, 26, 32, 37, 44, 46, 55, 60, 66, 74, 79, 96, 97; and

C.I. Reactive Blue 1, 2, 7, 14, 15, 23, 32, 35, 38, 41, 63, 80, 95.

[0073] As the dye, acid dyes or direct dyes are especially preferred because those have effects of improving the dissolution stability of the recording liquid and giving an excellent color tone, high water resistance and high photoresistance to a printed image.

[0074] The content of the dye as the colorant in the recording liquid is preferably 0.5 to 25 % by weight, more preferably 2 to 15 % by weight.

[0075] As the pigment for use in the present invention, an inorganic pigment or an organic pigment can be employed without a limitation on the type thereof. Since a pigment is not dissolved in a recording liquid but dispersed as particles therein in contrast to a dye, a recording liquid containing a pigment is not likely to penetrate deep into a paper as compared with a recording liquid containing a colorant other than a pigment and having the same penetration property. Thus, it is possible to obtain a high quality image with a high density and little strike-through.

[0076] As the inorganic pigment, titanium oxide, iron oxide, calcium carbonate, barium sulfate, aluminum hydroxide, barium yellow, cadmium red, or chrome yellow can be employed. In addition, a carbon black produced by a known method, such as a contact method, a furnace method, and a thermal method, can be also employed.

[0077] As the organic pigment, azo pigments (including azo lake, water-insoluble azo pigments, condensed azo pigments chelate azo pigments and so on); polycyclic pigments (such as phthalocyanine pigments, perylene pigments, perinone pigments, anthraquinone pigments, quinacrideone pigments, dioxazine pigments, indigo pigments, thioindigo pigments, isoindolinone pigments and quinophethalone pigments); dye chelates (such as basic dye-type chelates and acidic dye-type chelates); nitro pigments; nitroso pigments or aniline black can be employed. Above all, a pigment having a strong affinity for water is preferably employed. The content of the pigment as the colorant in the recording liquid is preferably 0.5 to 25 % by weight, more preferably 2 to 15 % by weight.

[0078] Examples of pigments preferably used in the present invention will be shown below but the present invention is not limited thereto. Examples of pigments for a black recording liquid include carbon blacks (C.I. pigment black 7) such as furnace black, lamp black, acetylene black, and channel black; metals such as copper, iron (C.I. Pigment Black 11), and titanium oxide; and organic pigments such as aniline black (C.I. Pigment Black 1).

[0079] Examples of pigments for a color recording liquid include

C.I. Pigment Yellow 1, 3, 12, 13, 14, 17, 24, 34, 35, 37, 42 (yellow iron oxide), 53, 55, 81, 83, 95, 97, 98, 100, 101, 104, 108, 109, 110, 117, 120, 138, 153;
C.I. Pigment Orange 5, 13, 16, 17, 36, 43, 51;
C.I. Pigment Red 1, 2, 3, 5, 17, 22, 23, 31, 38, 48:2, 48:2 (Permanent Red 2B (Ca)), 48:3, 48:4, 49:1, 52:2, 53:1, 57:1 (Brilliant Carmine 6B), 60:1, 63:1, 63:2, 64:1, 81, 83, 88, 101 (iron oxide red), 104, 105, 106, 108 (Cadmium Red), 112, 114, 122 (Quinacridone Magenta), 123, 146, 149, 166, 168, 170, 172, 177, 178, 179, 185, 190, 193, 209, 219;
C.I. Pigment Violet 1 (Rhodamine Lake), 3, 5:1, 16, 19, 23, 38;
C.I. Pigment Blue 1, 2, 15 (Phthalocyanine Blue), 15:1, 15:2, 15:3 (Phthalocyanine Blue) 16, 17:1, 56, 60, 63; and
C.I. Pigment Green 1, 4, 7, 8, 10, 17, 18, 36.

[0080] In the present invention, carbon black is preferably employed as the black pigment. As a pigment for a black recording liquid, carbon black is excellent in tone, has high water resistance, photoresistance and dispersion stability, and is inexpensive.

[0081] A graft pigment, which is a pigment (carbon, for example) surface-treated with a resin or the like so that the pigment may be dispersed in water, or a processed pigment, which is a pigment (carbon, for example) having a surface to which a functional group such as a sulfone group or a carboxyl group is added so that the pigment may be dispersed in water, may be also employed.

[0082] The pigment may be contained in microcapsules so that the pigment may be dispersed in water.

[0083] In the aqueous recording liquid according to the present invention preferably is dispersed a pigment having an average particle size in the range of 10 to 200 nm.

The term "average particle size" herein means a diameter at a cumulative volume of 50 %. The diameter at a cumulative volume of 50 % can be measured by a dynamic light scattering method (Doppler scattering light analytic method), in which laser beam is irradiated on a particle performing Brownian movement in a recording liquid and the diameter of the particle is obtained from a change in frequency of the light coming back from the particle (back scattered light).

[0084] As a grain size analyzer employing the system, Microtrac UPA 150 grain size analyzer manufactured by Honeywell Inc. can be used.

[0085] When a pigment is employed as the colorant, the resulting recording liquid has improved water resistance and photoresistance. Additionally, a phenomenon in which the recording liquid penetrates the layer of the recording medium to the reverse side thereof (which will be hereinafter referred to as "strike-through") can be prevented. Since

the pigment is not dissolved but dispersed in the recording liquid, the pigment component does not penetrate into the recording medium less than the liquid component of the recording liquid does but remains in a region adjacent the surface thereof when printing is conducted with an ink jet system. Thus, the image dries quickly and strike-through can be prevented.

[0086] When the average particle size of the pigment is less than 10 nm, the effect of preventing strike-through can not be obtained. When the average particle size is over 200 nm, the recording liquid has poor dispersion stability. Thus, the particle size is enlarged by aggregation and so on during storage so that the ejection stability of the recording liquid may be poor as compared with a pigment having an average particle size in the above range.

[0087] The pigment is preferably added to the recording liquid in the form of a pigment dispersion prepared by dispersing the pigment in an aqueous medium with the aid of a dispersant. As the dispersant, any conventionally known dispersant for use in preparation of a pigment dispersion such as hydrophilic polymers including natural polymers, semisynthetic polymers and pure synthetic polymers.

[0088] Examples of the natural polymer include a plant polymer such as Arabian gum, tragacanth gum, guar gum, karaya gum, locust bean gum, arabinogalactan, pectin, and quince seed starch;

a seaweed polymer such as alginic acid, carrageenen, and agar;

an animal polymer such as gelatin, casein, albumin, and collagen; and

a microbial polymer such as xanthene gum, and dextran.

[0089] Examples of the semisynthetic polymer include a cellulose polymer such as methyl cellulose, ethyl cellulose, hydroxy ethyl cellulose, hydroxy propyl cellulose, and carboxymethyl celllulose;

a starch polymer such as sodium starch glycolate, and sodium starch phosphate;

and a seaweed polymer such as sodium alginate, and propylene glycol ester alginate.

[0090] Examples of the pure synthetic polymer include polyacrylic acid, polymethacrylic acid, acrylic acid-acrylonitrile copolymer, vinyl acetate-acrylic ester copolymer, acrylic acid-alkyl acrylate copolymer, styrene-acrylic acid copolymer, styrene-methacrylic acid copolymer, styrene-acrylic acid-alkyl acrylate copolymer, styrene-methacrylic acid-alkyl acrylate copolymer, styrene-α-methylstyrene-acrylic acid copolymer, copolymer of styrene-α-methylstyrene-acrylic acid copolymer with alkyl acrylate, styrene-maleic acid copolymer, vinylnaphthalene-maleic acid copolymer, vinyl acetate-ethylene copolymer, vinyl acetate-fatty acid vinylethylene copolymer, vinyl acetate-maleic ester copolymer, vinyl acetate-crotonic acid copolymer, and vinyl acetate-acrylic acid copolymer.

[0091] The average molecular weight of the copolymer is preferably about 3,000 to 50,000, more preferably about 5,000 to 30,000, most preferably about 7,000 to 15,000. The polymeric dispersant may be added in any amount as long as the pigment can be stably dispersed and the other effects of the present invention are not lost.

[0092] The weight ratio of the pigment to the dispersant is about 1:0.06 to 1:3, more preferably about 1:0.125 to 1:3.

[0093] A water-soluble surfactant may be also used as the pigment dispersant. Since a water-soluble surfactant increases less viscosity of the recording liquid than the same amount of a polymeric dispersant does, a pigment ink which exhibits good ejection property when used in ink jet recording system can be easily obtained.

[0094] Specific examples of water-soluble surfactants usable as a pigment dispersant include anionic surfactants such as alkylallyl, alkylnaphthalene sulfonate, alkyl phosphate, alkyl sulfate, alkyl sulfonate, alkylether sulfate, alkyl sulfosuccinate, alkyl ester sulfate, alkylbenzen sulfonate, alkyldiphenyl ether disulfonate, alkyl arylether phosphate, alkyl arylether sulfate, alkyl arylether ester sulfate, olefin sulfonate, alkane olefin sulfonate, polyoxyethylene alkyl ether phosphate, polyoxyethylene alkylether ester sulfate, ether carboxylate, sulfosuccinate, α-sulfo fatty acid ester, fatty acid salts, a condensate of a higher fatty acid with an amino acid, and naphthenate;

cationic surfactants such as alkylamine salts, dialkylamine salts, aliphatic amine salts, benzalkonium salts, quaternary ammonium salts, alkylpyridinium salts, imidazolinium salts, sulfonium salts, and phosphonium salts;

nonionic surfactant such as polyoxyethylene alkyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene alkylphenyl ether, polyoxyethylene glycol ester, polyoxyethylene fatty acid amide, polyoxyethylene fatty acid ester, polyoxyethylene polyoxypropylene glycol, glyceroester, sorbitan ester, sucrose ester, polyoxyethylene ether of glyceroester, polyoxyethylene ether of sorbitan ester, polyoxyethylene ether of sorbitol ester, aliphatic alkanolamid, amine oxide, polyoxyethylene alkylamine, glycerin fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, and alkyl (poly)glycoxyde; and

ampholytic surfactant such as imidazoline derivatives including imidazolinium betaine; dimethylalkyllauryl betaine, alkylglycine, and alkyldi(aminoethyl)glycine.

[0095] The surfactant as the dispersant may be added in any amount as long as the pigment can be stably dispersed and the other effects of the present invention are not lost.

[0096] More preferably, the dispersant for the recording liquid has a carboxyl group. When the dispersant has a carboxyl group, not only the dispersion stability is improved but also a high printing quality can be obtained. Additionally, there can be obtained effects of enhancing water resistance of the recording medium after printing and preventing strike-through as mentioned before. Especially, when a pigment dispersed with a dispersant having a carboxyl group is used together with the components (A) and (B), a sufficient drying rate and an effect of decreasing strike-through

can be obtained even when printing is conducted on a recording medium having a relatively high sizing degree such as a plain paper. The reason of this is assumed to be as follows; Since the dissociation constant of carboxylic acid is smaller than those of other acid groups, when the solubility of the dispersant is lowered due to decrease of pH of the recording liquid and an interaction with ions of polyvalent metals such as calcium present in a region adjacent a surface of the recording medium after the pigment has adhered to the recording medium, the dispersant itself and the pigment are aggregated.

[0097] Preferably, in the aqueous recording liquid according to the present invention, a pigment having a modified surface to which a carboxyl group is bonded is dispersed in water. In this case, since the pigment has a modified surface to which a carboxyl group is bonded, not only the dispersion stability is improved but also a high printing quality can be obtained by similar functions as above and the water resistance of the recording medium after printing is much improved. Additionally, an aqueous recording liquid of this type has high redispersibiliry after drying. Thus, it causes no clogging of a nozzle of an ink jet head and allows printing with good printing quality with a simple cleaning operation even when water in the recording liquid in the vicinity of the nozzle is evaporated during a long time suspension of printing operation.

[0098] The aqueous recording liquid according to the present invention is applicable to bar code printing and postmark printing using an invisible recording liquid, which are rapidly spreading in recent years. In this case, an infrared absorber or an ultraviolet absorber having absorption not in visible region but in infrared region or ultraviolet region is added in the recording liquid instead of an ordinary dye or pigment.

[0099] The aqueous recording liquid according to the present invention may contain conventionally known additives in addition to the colorant, the wetting agent and the surfactant in such an amount that does not deteriorate the effects of the present invention.

[0100] For example, the aqueous recording liquid according to the present invention may contain a resin emulsion. The resin emulsion usable herein comprises water as a continuous phase and a resin component as shown below as a dispersed phase.

[0101] Examples of the resin component as the dispersed phase include acrylic resin, vinyl acetate resin, styrene-butadiene resin, vinyl chloride resin, acryl-styrene resin, butadiene resin, and styrene resin. The resin is preferably a polymer having both a hydrophilic segment and a hydrophobic segment. The particle size of the resin component is not particularly limited as long as the resin component can form an emulsion but is preferably not more than about 150 nm, more preferably about 5 to 100 nm.

[0102] The resin emulsion can be obtained by mixing resin particles into water, together with a surfactant as desired.

[0103] Examples of commercially available resin emulsions include Microgel E-1002 and E-5002 (emulsion of styrene-acryl resin, manufactured by Nippon Paint Co., Ltd.), Voncoat 4001 (emulsion of acrylic resin, manufactured by Dainippon Ink and Chemicals, Inc.), Voncoat 5454 (emulsion of styrene-acryl resin, manufactured by Dainippon Ink and Chemicals, Inc.), SAE-1014 (emulsion of styrene-acryl resin, manufactured by Nippon Zeon Co., Ltd.), and Saivinol SK-200 (emulsion of acrylic resin, manufactured by Saiden Chemical Industry Co., Ltd).

[0104] The aqueous recording liquid according to the present invention preferably contains a resin emulsion in an amount of 0.1 to 40 % by weight, more preferably 1 to 25% by weight, based on a total weight of the aqueous recording liquid.

[0105] The resin emulsion has properties of increasing viscosity and aggregating so that it has effects of inhibiting the penetration of a coloring component in the depth direction of a paper and accelerating the fixation of the colorant component on the recording medium. Some resin emulsions have an additional effect of forming a film on the recording medium which improves the scratch resistance of a printed image.

[0106] The recording liquid composition of the aqueous recording liquid according to the present invention may contain a saccharide such as monosaccharides, disaccharides, oligosaccharides (including trisaccharides and tetrasaccharides), and other polysaccharides for the purpose of preventing evaporation of water and so on. Preferred examples include glucose, mannose, fructose, ribose, xylose, arabinose, galactose, maltose, cellobiose, lactose, sucrose, trehalose, and maltotriose. The term "polysaccharides" used herein means saccharides in the broad sense as including substances which exist widely in the world of nature, such as α-cyclodextrin, and cellulose.

[0107] Derivatives of these saccharides usable herein include reducing sugars of the above saccharides (for example, sugar alcohols represented by the general formula $HOCH_2(CHOH)_nCH_2OH$, wherein n is an integer of 2 to 5), oxidizing sugars (for example, aldonic acid or uronic acid), amino acids, and thioic acid. Above all, sugar alcohols are particularly preferred, and specific examples thereof include maltitol and sorbitol.

[0108] The content of the saccharide is 0.1 to 40 % by weight, preferably 0.5 to 30 % by weight, based on the amount of the recording liquid composition.

[0109] The aqueous recording liquid according to the present invention may contain sodium alginate. Sodium alginate is a hydrophilic polyelectrolyte which is contained in only blown algae and which is present as a cell membrane material or an intercellular material. In a chemical sense, it is a polymer of D-mannuronic acid [M] which is polymerized through β-1 and 4 bonds and L-guluronic acid [G] which polymerized through α-1 and 4 bonds and has viscosity-increasing

effect, stabilizing effect, dispersing effect, gelatinization effect, film-forming effect and so on. When added in an ink jet recording liquid, sodium alginate causes a change in pH of the recording liquid to change in viscosity thereof, deposition of salts, gelatinization with multivalent cations, and thus can prevent blur of a single color (feathering) and blur between different colors.

[0110] The aqueous recording liquid according to the present invention may contain an antiseptic and antifungal agent such as sodium dehydroacetate, sodium sorbate, 2-pyridinethiol-1-oxide sodium, sodium benzoate, sodium pentachlorophenol, or the like.

[0111] The aqueous recording liquid according to the present invention may contain any substance as a pH regulator as long as it can adjust the pH of the aqueous recording liquid to a desired value without giving an adverse effect on the aqueous recording liquid.

[0112] Examples of such substances include amines such as diethanolamine and triethanolamine; a hydroxide of an alkali metal element such as lithium hydroxide, sodium hydroxide and potassium hydroxide; ammonium hydroxide; quaternary ammonium hydroxide; quaternary phosphonium hydroxide; and a carbonate of an alkali metal element such as lithium carbonate, sodium carbonate and potassium carbonate.

[0113] Examples of chelate reagents include sodium ethylenediaminetetraacetate, sodium nitrilotriacetate, sodium hydroxyethyl ethylenediaminetriacetate, sodium diethylenetriaminepentaacetate and sodium uramild iacetate.

[0114] The aqueous recording liquid according to the present invention may contain a rust preventive such as acid sulfite, sodium thiosulfate, ammonium thiodiglycolate, diisopropyl ammonium nitrate, pentaerythritol tetranitrate, dicyclohexyl ammoium nitrate or the like.

[0115] The aqueous recording liquid may contain a water-soluble ultraviolet absorber depending upon the purpose thereof.

[0116] The aqueous recording liquid according to the present invention can be preferably used in an ink jet recording system for forming a color image on a recording medium by ejecting or jetting an aqueous recording liquid from a minute ejection port onto the recording medium. It is, however, needless to say that the aqueous recording liquid according to the present invention can be also used as a recording liquid for general writing utensils such as an aqueous ink pen, aqueous ink marker, aqueous ink ball point pen, a recorder, and a pen plotter. Additionally, the aqueous recording liquid according to the present invention is not limited to the above usage.

[0117] The aqueous recording liquid according to the present invention must be adjusted to a desired viscosity when used in ink jet recording system. The viscosity of the aqueous recording liquid must be varied depending on the ejecting force of a head but preferably not greater than 10 mP·a in general. When the viscosity is greater than 10 mP·a, the aqueous recording liquid can not be sufficiently ejected by an ink jet system and tends to cause image deterioration.

[0118] A recording method preferably employed as a recording method of the present invention is a method in which thermal energy corresponding to a recording signal is applied to the recording liquid to generate droplets thereof, with which an image is formed on a recording medium.

[0119] Preferably, the recording medium is mainly composed of pulp fibers and has a sizing degree of at least 50s and an air-permeability of 5 to 50s. When printing is conducted on both sides of such a recording medium using the aqueous recording liquid according to the present invention, the image printed on the reverse side of the recording medium never interferes with recognition of the image printed on the front side thereof. The sizing degree herein is a value measured according to the Steckigt sizing degree testing method of JIS P8122-76 and the air-permeability herein is a value measured according to air-permeability testing method of JIS P8117-80.

[0120] When the sizing degree is less than 10s, the recording liquid penetrates to the reverse side of the recording medium and strike-through occurs. When the permeability is less than 5s, the recording liquid also penetrates to the reverse side of the recording medium and strike-through occurs. A recording medium having a sizing degree of greater than 50s causes no problem in the printing quality and the drying property of the recording liquid but expensive because it contains a filler more than necessary.

[0121] Also, when a recording medium having a sizing degree and an air-permeability outside the above range is used in an electronic copying machine or printer, the filler is transferred to a photoreceptor or a fixing roller, causing deterioration of image quality or a breakdown of the machine. Thus, users must use papers designed specifically for ink jet recording, which requires the users to use different types of papers depending upon the type of a machine, imposing a burden upon the users. When a recording medium having a sizing degree and an air-permeability in the above range is employed, the user can deal with it in the same way as in other non-coated plain papers such as a transfer paper for electrophotography, a printing paper, a typewriter paper, a wire dot printer paper, a word processor paper, a letter paper, and a reporting paper so that the user does not have to distinguish a paper for ink jet recording from other plain papers. With respect to the production, the recording medium can be produced using an existing paper making machine with a minimum equipment investment. Also, the recording medium can be commonly applied to uses of other recording system.

[0122] As the material of pulp fibers for use in the present invention, any pulp can be used irrespective of the type and treatment method thereof as long as it has no adverse effect on an ink jet recording system. Non-wood pulp (kenuf

pulp, flux pulp, bamboo pulp, seaweed pulp or the like) or recycled paper pulp can be added, or may be used as the main component. A preferred example is a chemical pulp represented by LBKP and NBKP. These pulps are made into papers by an ordinary method as is the case with a general plain paper, using a known sizing agent, a filler and other paper-making aids as necessary.

[0123] Examples of the sizing agent include rosin size, AKD, sodium chloride, potassium chloride, stylene-maleic acid copolymer, quaternary ammonium salts, alnickel succinic anhydride, petroleum resin-based sizes, epichlorohidon, cationic starch, and acrylamide.

[0124] Examples of the filler include clay, calcium carbonate, talc, titanium dioxide, and synthetic silica.

[0125] Also, a paper strengthening agent, a yield improver, a fixing agent, a dye and other paper-making aids may be added.

[0126] As a result of zealous studies, the present inventor have found that, when printing is conducted under the condition that an ejection volume per droplet (V) ejected from an recording head satisfies the equation (3), a high-quality image with little strike-through, a uniformity in solid part and without a white void;

$$2.5 \times 10^8/R^{2.6} \leq V \leq 6.0 \times 10^8/R^{2.6} \quad (3)$$

wherein R is a density at which ink droplets are dotted in recording on a recording medium mainly composed of pulp fibers and having a sizing degree of at least 10s and air-permeability of 5 to 50s and expressed by a number of dots per a unit length using a unit of dpi (Dot Per Inch). In some serial type ink jet printers, the dot density in a scanning direction (main scanning direction) and the dot density in a paper transporting direction (sub-scanning direction) are different. In such a case, a value obtained by calculating such that the number of dots in the main scanning direction and the number of the dots in the sub-scanning direction may be the same in a unit area.

[0127] The left side of the equation (3) shows a relation suitable for obtaining a high-quality image with a high density and without a white streak when a solid image is printed a plain paper. The right side of the equation (3) shows a relation suitable for preventing an increase of strike-through and occurrence of blur caused by adhering an excessive amount of the recording liquid. Neither of the relations can be established without the excellent penetrability for a plain paper of the recording liquid according to the present invention.

[0128] The recording liquid according to the present invention, which has high penetrability and thus allows printing of a high quality image without blur, can be applied to a high-speed recording process, which was difficult to accomplish with an ordinary recording liquid. Namely, in a recording method of forming an image on a recording medium by ejecting and jetting a plurality of aqueous recording liquids as droplets from one ejection nozzle or separated ejection nozzles such that at least a part of adjacent pixel areas are overlapped on the recording medium, when the two droplets of the aqueous recording liquids which forms the pixel areas to be partially overlapped on the recording medium are ejected with a time difference of not greater than 0.125 ms, a extremely high speed printing can be accomplished.

[0129] In recent years, the technology concerning an ink jet printer has significantly progressed and the printing speed has been improved. However, in order to maintain the image quality above a certain level, two adjacent dots are not continuously formed but one of the dots is not formed until the other has penetrated into the paper. Namely, high quality printing is accomplished by a method called multipass printing, sacrificing the printing speed. The aqueous recording liquid according to the present invention exhibits high penetration property and thus allows printing of a high quality image by single-pass printing, which was conventionally impossible.

[0130] Description will be hereinafter made of a recording liquid cartridge containing the aqueous recording liquid according to the present invention and an ink jet recording apparatus including the recording liquid cartridge with reference to the appended drawings. The following is only one example and is not intended to limit the present invention.

[0131] Fig. 1 is a schematic front view of a mechanism section of a serial type ink jet recording apparatus mounting an ink cartridge having a recording liquid containing part containing the recording liquid according to the present invention.

[0132] The mechanism section of the ink jet recording apparatus has side plates 1 and 2 on both sides thereof and a main support guide rod 3 and a sub-support guide rod 4 extending generally horizontally between the side plates 1 and 2. A carriage unit 5 is supported by the main support guide rod 3 and the sub-support guide rod 4 for sliding movement in a main scanning direction. Four heads 6 each for ejecting a yellow (Y) ink, a magenta (M) ink, a cyan (C) ink and a black (Bk) ink are mounted on the carriage unit 5 with ejection surfaces 6a (nozzle surfaces) thereof facing down. Four ink cartridges 7y, 7m, 7c, and 7k, each of which is a ink supplying body for supplying the respective ink to the corresponding head 6, are exchangeably mounted above each of the heads 6 of the carriage unit 5. The carriage unit 5 is connected to a timing belt 11 stretched between a driving pulley (driving timing pulley) 9, which is rotated by a main scanning motor 8, and a driven pulley (idler pulley) 10. By driving the main scanning motor 8, the carriage unit 5, namely the four heads 6 are moved in the main scanning direction.

[0133] Sub-frames 13 and 14 are erected on a bottom plate 12 connecting the side plates 1 and 2. A transporting roller 15 for feeding a paper 16 in a sub-scanning direction, which is perpendicular to the main scanning direction, is rotatably supported between the sub-frames 13 and 14. A sub-scanning motor 17 is arranged aside the sub-frame 14. A gear 18 fixed on a rotating shaft of the sub-scanning motor 17 and a gear 19 fixed on the transporting roller 15 are provided so as to transmit rotation of the sub-scanning motor 17 to the transporting roller 15.

[0134] Between the side plate 1 and the sub-frame 12 is arranged a reliability maintaining/recovering mechanism 21 (which will be hereinafter referred to as "sub-system"). The sub-system 21 has a holder 23 for holding four capping means 22 for capping ejection surfaces 6a of the heads 6, respectively. The holder 23 is swingably held by linking members 24.

[0135] When the carriage unit 5 is moved in the main scanning direction and brought into contact with an engaging portion 25 provided on the holder 23, the holder 23 is lifted up along with the movement of the carriage unit 5 and the ejection surfaces 6a of the ink jet heads 6 are capped with the capping means 22. When the carriage unit 5 is moved to the side of a printing area, the holder 23 is lifted down along with the movement of the carriage unit 5, whereby the capping means 22 are removed from the ejection faces 6a of the ink jet heads 6.

[0136] Each of the capping means 22 is connected to a suction pump 22 via a suction tube 26 and has an open air port communicated with the atmosphere via an open air tube and an open air valve. The suction pump 22 discharges sucked waste liquid into a waste liquid tank (not shown) via a drain tube or the like.

[0137] On one side of the holder 23, a blade arm 29 carrying a wiper blade 28, which is wiping means comprising an elastic material such as fiber, a foam or a rubber, for wiping the ejection surfaces 6a of the ink jet heads 6 is swingably pivoted. The blade arm 29 is swung by rotation of a cam which is rotated by driving means (not shown).

[0138] Description will be next made of an ink cartridge 7 with reference to Fig. 2 and Fig. 3. Fig. 2 is a perspective view of an external appearance of the ink cartridge before being loaded in the recording apparatus and Fig. 3 is a front cross-sectional view of the ink cartridge.

[0139] As shown in Fig. 3, the ink cartridge 7 comprises a cartridge body 41 accommodating an ink absorber 42 containing an ink of a required color. The cartridge body 41 comprises a case 43 having a wide opening at a top part thereof and an upper cover member 44 melt-bonded or adhered over the opening, and made of, for example, a resin molded product. The ink absorber 42 comprises a porous body such as urethane foam and is inserted into the cartridge body 41 under compression. Then, the ink is poured into the cartridge body 41 such that the ink absorber 41 may absorb the ink.

[0140] The case 43 of the cartridge body 41 has a bottom having an ink supply port 45 for supplying the ink to the recording head 6. The ink supply port 45 has an inner circumference surface on which a seal ring 46 is fitted. The upper cover member 44 has an open air port 47.

[0141] The cartridge body 41 has a cap member 50 for closing the ink supply port 45 before the cartridge 7 is loaded into the printer in order to prevent the ink from leaking when the case 43 is deformed by a pressure exerted on side walls thereof having a relatively large width at the time of treating the cartridge such as loading into the printer or transporting, or at the time of vacuum packing.

[0142] As shown in Fig. 2, a film-like seal member 55 having an oxygen permeability of not less than 100 ml/m^2 is adhered on the upper cover member 44, whereby the open air port 47 is sealed. The seal member 55 is so sized as to seal a plurality of grooves 48 formed around the open air port 47 together with the open air port 47. When the open air port 47 is sealed with the seal member 55 having an oxygen permeability of not less than 100 ml/m^2 and the ink cartridge 7 is packaged with a packaging material having no air permeability such as an aluminum-laminated film under a reduced pressure, even if gas is dissolved in the ink at the time of filling the ink or by air contained in a space A (see Fig. 3) formed between the ink absorber 42 and the cartridge body 41, the air dissolved in the ink is discharged into a space high in vacuum degree between the cartridge body 41 and the packaging member through the seal member 55, thereby enhansing deaeration degree of the ink.

[0143] One embodiment of a recording liquid containing part containing the recording liquid according to the present invention and a recording cartridge having a head part for ejecting droplets of the recording liquid is shown in Fig .4 and description thereof will be hereinafter made.

[0144] A recording unit 30 is a serial type recording unit and has a main part comprising an ink jet head 6, an ink tank 41 containing a recording liquid to be supplied to the ink jet head 6, and a cover member for airtightly closing the ink tank 41. A multiplicity of nozzles 32 for ejecting the recording liquid are formed in the ink jet head 6. The recording liquid is introduced from the ink tank 41 through an ink supply tube (not shown) to a common liquid chamber (not shown) and ejected from the nozzles 32 in response to electric signals from a main body inputted through an electrode 31. The recording unit of this type has a structure suitable for a head which can be produced at a low price, namely a head using thermal energy as power source for driving, called thermal system or bubble system head. The recording liquid of the present invention has an improved wettability to a thermal element of a bubble or thermal recording system by containing the component (A). Also, the component (A) imparts high ejection stability and frequency stability to the recording liquid with a small amount so that the recording liquid has high safety. Therefore, the recording liquid according

to the present invention is highly suitable for such recording systems.

[0145] Description has been herein made taking a serial type ink jet recording apparatus as an example, the recording liquid according to the present invention is applicable to a recording apparatus having a so-called line head in which a plurality of nozzles are integrated at a density equivalent to or in a fraction of a resolution that of an purposed image and arranged in an arbitrary fashion such as a zigzag fashion and in a width which is greater than that of a recording medium.

[0146] The recording apparatus herein may be a multifunction apparatus combined with a fax machine, a scanner and so on as well as an output printer for a PC or a digital camera.

[0147] Examples and comparative examples of the present invention will be hereinafter shown but those are not intended to limit the present invention. Percentages are by weight.

Example 1

[0148] The following ink ingredients were mixed and stirred. The mixture was adjusted to pH 8 with 10 % aqueous solution of lithium hydroxide and then filtered with a membrane filter having an average aperture size of 0.1 μm, thereby obtaining an ink composition 1.

Ink composition 1	
C.I. Direct Black 168	4 %
Glycerin	5 %
Ethylene glycol	5 %
Compound (1-4)	0.3 %
2,2,4-Trimethyl-1,3-pentanediol	1 %
Ion-exchanged water	Balance

Example 2

[0149] An ink composition 2 was prepared in the same manner as in Example 1 except that the following compositions were used and that the mixture was adjusted to pH 7.5 with sodium hydroxide.

Ink composition 2	
C.I. Direct Yellow 142	3.0 %
Thiodiglycol	8 %
Compound (1-5)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
Ion-exchanged water	Balance

Example 3

[0150] An ink composition 3 was prepared in the same manner as in Example 1 except that the following compositions were used and that the mixture was adjusted to pH 8 with 10 % aqueous solution of lithium hydroxide.

Ink composition 3	
C.I. Direct Red 227	3 %
Thiodiglycol	8 %
Compound (1-6)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	2 %
Ion-exchanged water	Balance

Example 4

[0151] An ink composition 4 was prepared in the same manner as in Example 1 except that the following compositions were used and that the mixture was adjusted to pH 9 with 10 % aqueous solution of lithium hydroxide.

Ink composition 4	
C.I. Direct Blue 199	3 %
Thiodiglycol	8 %
Compound (1-5)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
Ion-exchanged water	Balance

Example 5

[0152] The following ingredients of a dispersion were mixed using a bead mill, whereby carbon black was dispersed therein. The thus obtained aqueous dispersion was mixed and stirred with the other ink ingredients. The mixture was adjusted to pH 8 with 10 % aqueous solution of lithium hydroxide and then filtered with a membrane filter having an average aperture size of 0.8 μm, thereby obtaining an ink composition 5.

Pigment dispersion 1	
Carbon black (average particle size: 104 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 5	
Pigment dispersion 1	33.3 %
Diethylene glycol	6.5 %
Glycerin	3.5 %
Compound (1-1)	0.3 %
Compound (1-3)	0.1 %
25 % Aqueous solution of compound (13-3)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	2 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 6

[0153] A pigment dispersion 2 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 2, an ink composition 6 was obtained.

Pigment dispersion 2	
Carbon black (average particle size: 104 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 6	
Pigment dispersion 2	33.3 %
Ethylene glycol	6.5 %
N-methyl-2-pyrolidone	3.5 %
Compound (1-1)	0.3 %
25 % Aqueous solution of compound (13-4)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	3 %

(continued)

Ink composition 6	
2-Pyrolidone	2 %
Alkyl ester fluoride; nonionic surfactant	0.3 %
Ion-exchanged water	Balance

Example 7

[0154] A pigment dispersion 3 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 3, an ink composition 7 was obtained.

Pigment dispersion 3	
Carbon black (average particle size: 99 nm)	15 %
Formalin condensate of naphthalene sulfonate	3 %
Ion-exchanged water	Balance

Ink composition 7	
Pigment dispersion 3	33.3 %
Polyethylene glycol (molecular weight: 200)	15 %
Compound (1-3)	0.05 %
25 % Aqueous solution of compound (13-2)	0.1 %
2,2,4-Trimethyl-1,3-pentanediol	5 %
Alkyl ester fluoride; nonionic surfactant	0.3 %
Ion-exchanged water	Balance

Example 8

[0155] A pigment dispersion 4 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 4, an ink composition 8 was obtained.

Pigment dispersion 4	
C.I. Pigment Yellow 13 (average particle size: 117 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 8	
Pigment dispersion 4	33.3 %
Glycerin	5 %
Diethylene glycol	10 %
Compound (1-2)	0.3 %
25 % Aqueous solution of compound (13-4)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 9

[0156] A pigment dispersion 5 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 5, an ink composition 9 was obtained.

Pigment dispersion 5	
C.I. Pigment Yellow 74 (average particle size: 96 nm)	15 %
Formalin condensate of naphthalene sulfonate	3 %
Ion-exchanged water	Balance

Ink composition 9	
Pigment dispersion 5	33.3 %
Polyethylene glycol (molecular weight: 200)	10 %
Compound (1-7)	0.05 %
2,2,4-Trimethyl-1,3-pentanediol	5 %
Ion-exchanged water	Balance

Example 10

[0157] A pigment dispersion 6 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 6, an ink composition 10 was obtained.

Pigment dispersion 6	
C.I. pigment red 122 (average particle size: 120 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 10	
Pigment dispersion 6	33.3 %
Glycerin	5 %
Ethylene glycol	10 %
Compound (1-1)	0.3 %
25 % Aqueous solution of compound (13-4)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	2 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 11

[0158] A pigment dispersion 7 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 7, an ink composition 11 was obtained.

Pigment dispersion 7	
C.I. pigment red 57:1 (average particle size: 115 nm)	15 %
Formalin condensate of naphthalene sulfonate	3 %
Ion-exchanged water	Balance

Ink composition 11	
Pigment dispersion 7	33.3 %
Polyethylene glycol (molecular weight: 200)	10 %
Compound (1-8)	0.05 %
2-Methyl-1,3-hexanediol	1 %

(continued)

Ink composition 11	
2,2,4-Trimethyl-1,3-pentanediol	1 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 12

[0159] A pigment dispersion 8 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 8, an ink composition 12 was obtained.

Pigment dispersion 8	
C.I. Pigment Blue 15:3 (average particle size 123 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 12	
Pigment dispersion 8	33.3 %
Glycerin	3 %
1,5-pentanediol	15 %
Compound (1-4)	0.3 %

25 % Aqueous solution of compound (13-4)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	5 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 13

[0160] A pigment dispersion 9 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 9, an ink composition 13 was obtained.

Pigment dispersion 9	
C.I. Pigment Blue 56 (average particle size: 138 nm)	15 %
Formalin condensate of naphthalene sulfonate	3 %
Ion-exchanged water	Balance

Ink composition 13	
Pigment dispersion 9	33.3 %
Polyethylene glycol (molecular weight: 200)	10 %
Compound (1-9)	0.05 %
2,2,4-Trimethyl-1,3-pentanediol	4 %
Triethylene glycol monobutyl ether	2 %
Ion-exchanged water	Balance

Example 14

[0161] An ink composition 14 was obtained in the same manner as in Example 1 except that the following compo-

sitions were used.

Ink composition 14	
Carboxyl group-bonded carbon black dispersion (solid content; 16.4 % by weight, average particle size; 128 nm)	33.3 %
Diethylene glycol	15 %
Glycerin	5 %
Compound (1-4)	0.8 %
2,2,4-Trimethyl-1,3-pentanediol	2 %
N-methyl-2-pyrolidone	2 %
Ion-exchanged water	Balance

Example 15

[0162] An ink composition 15 was obtained in the same manner as in Example 1 except that the following compositions were used.

Ink composition 15	
Carboxyl group-bonded carbon black dispersion (solid content 16.4 % by weight, average particle size 128 nm)	33.3 %
Ethylene glycol	15 %
Compound (1-1)	1 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
N-methyl-2-pyrolidone	2 %
Ion-exchanged water	Balance

Example 16

[0163] An ink composition 16 was obtained in the same manner as in Example 1 except that the following compositions were used.

Ink composition 16	
Sulfonic group-bonded carbon black dispersion (solid content 18 % by weight,average particle size 132 nm)	33 %
1,5-Pentanediol	5 %
N-methyl-2-Pyrolidone	2 %
Compound (1-6)	1 %
2,2,4-Trimethyl-1,3-pentanediol	1 %
Ion-exchanged water	Balance

Example 17

[0164] An ink composition 17 was obtained in the same manner as in Example 1 except that the following compositions were used.

Ink composition 17	
Sulfonic group-bonded carbon black dispersion (solid content 18 % by weight,average particle size 132 nm)	33 %
1,5-Pentanediol	5 %
N-methyl-2-pyrolidone	2 %

(continued)

Ink composition 17	
Compound (1-1)	1 %
2,2,4-Trimethyl-1,3-pentanediol	1.5 %
Ion-exchanged water	Balance

Example 18

[0165] A pigment dispersion 10 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 10, an ink composition 18 was obtained.

Pigment dispersion 10	
Carbon black (average particle size 53 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 18	
Pigment dispersion 10	33.3 %
Polyethylene glycol (molecular weight: 200)	5 %
Ethylene glycol	30 %
Compound (1-5)	0.01 %
2,2,4-Trimethyl-1,3-pentanediol	8 %
Ion-exchanged water	Balance

Example 19

[0166] A pigment dispersion 11 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 11, an ink composition 19 was obtained.

Pigment dispersion 11	
Carbon black (average particle size 196 nm)	15 %

Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 19	
Pigment dispersion 11	33.3 %
1,5-Pentanediol	5 %
N-methyl-2-pyrolidone	6.5 %
Compound (1-3)	4 %
2,2,4-Trimethyl-1,3-pentanediol	5 %
Ion-exchanged water	Balance

Example 20

[0167] An ink composition 20 was prepared in the same manner as in Example 1 except that the following compositions were used and that the mixture was adjusted to pH 8 with sodium hydroxide.

Ink composition 20	
C.I. Direct Black 168	4 %
Glycerin	5 %
Ethylene glycol	5 %
Compound (2-4)	0.3 %
2,2,4-Trimethyl-1,3-pentanediol	1 %
Ion-exchanged water	Balance

Example 21

[0168] An ink composition 21 was prepared in the same manner as in Example 1 except that the following compositions were used and that the mixture was adjusted to pH 7.5 with sodium hydroxide.

Ink composition 21	
C.I. Direct Yellow 142	3.0 %
Thiodiglycol	8 %
Compound (2-1)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
Ion-exchanged water	Balance

Example 22

[0169] An ink composition 22 was prepared in the same manner as in Example 1 except that the following compositions were used and that the mixture was adjusted to pH 8 with 10 % aqueous solution of lithium hydroxide.

Ink composition 22	
C.I. Direct Red 227	3 %
Thiodiglycol	8 %
Compound (2-3)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	2 %
Ion-exchanged water	Balance

Example 23

[0170] An ink composition 23 was prepared in the same manner as in Example 1 except that the following compositions were used and that the mixture was adjusted to pH 9 with 10 % aqueous solution of lithium hydroxide.

Ink composition 23	
C.I. Direct Blue 199	3 %
Thiodiglycol	8 %
Compound (2-3)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
Ion-exchanged water	Balance

Example 24

[0171] A pigment dispersion 12 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 12, an ink composition 24 was obtained.

Pigment dispersion 12	
Carbon black (average particle size: 104 nm)	15 %

(continued)

Pigment dispersion 12	
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 24	
Pigment dispersion 12	33.3 %
Diethylene glycol	6.5 %
Glycerin	3.5 %
Compound (2-1)	0.3 %
Compound (2-4)	0.1 %
25 % Aqueous solution of compound (13-3)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	2 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 25

[0172] A pigment dispersion 13 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 13, an ink composition 25 was obtained.

Pigment dispersion 13	
Carbon black (average particle size: 104 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 25	
Pigment dispersion 13	33.3 %
Ethylene glycol	6.5 %
N-methyl-2-Pyrolidone	3.5 %
Compound (2-3)	0.3 %
25 % Aqueous solution of compound (13-4)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
2-Pyrolidone	2 %
Alkyl ester fluoride; nonionic surfactant	0.3 %
Ion-exchanged water	Balance

Example 26

[0173] A pigment dispersion 14 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 14, an ink composition 26 was obtained.

Pigment dispersion 14	
Carbon black (average particle size: 99 nm)	15 %
Formalin condensate of naphthalene sulfonate	3 %
Ion-exchanged water	Balance

Ink composition 26	
Pigment dispersion 14	33.3 %
Polyethylene glycol (molecular weight: 200)	15 %
Compound (2-1)	0.05 %
25 % Aqueous solution of compound (13-2)	0.1 %
2,2,4-Trimethyl-1,3-pentanediol	5 %
Alkyl ester fluoride; nonionic surfactant	0.3 %
Ion-exchanged water	Balance

Example 27

[0174] A pigment dispersion 15 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 15, an ink composition 27 was obtained.

Pigment dispersion 15	
C.I. Pigment Yellow 13 (average particle size: 117 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 27	
Pigment dispersion 15	33.3 %
Glycerin	5 %
Diethylene glycol	10 %
Compound (2-5)	0.3 %
25 % Aqueous solution of compound (13-4)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 28

[0175] A pigment dispersion 16 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 16, an ink composition 28 was obtained.

Pigment dispersion 16	
C.I. Pigment Yellow 74 (average particle size: 96 nm)	15 %
Formalin condensate of naphthalene sulfonate	3 %
Ion-exchanged water	Balance

Ink composition 28	
Pigment dispersion 16	33.3 %
Polyethylene glycol (molecular weight: 200)	10 %
Compound (2-4)	0.05 %
2,2,4-Trimethyl-1, 3-pentanediol	5 %
Ion-exchanged water	Balance

Example 29

[0176] A pigment dispersion 17 was prepared in the same manner as in Example 5 except that the following com-

positions were used. Using the thus obtained pigment dispersion 17, an ink composition 29 was obtained.

Pigment dispersion 17	
C.I. Pigment Red 122 (average particle size: 120 nm)	15 %
Styrene-acrylate-diethanolamine methacrylateterpolymer	3 %
Ion-exchanged water	Balance

Ink composition 29	
Pigment dispersion 17	33.3 %
Glycerin	5 %
Ethylene glycol	10 %
Compound (2-2)	0.3 %
25 % Aqueous solution of compound (13-4)	0.5 %
2,2,4-Trimethyl-1,3-pentanediol	2 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 30

[0177] A pigment dispersion 18 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 18, an ink composition 30 was obtained.

Pigment dispersion 18	
C.I. Pigment Red 57:1 (average particle size: 115 nm)	15 %
Formalin condensate of naphthalene sulfonate	3 %
Ion-exchanged water	Balance

Ink composition 30	
Pigment dispersion 18	33.3 %
Polyethylene glycol (molecular weight: 200)	10 %
Compound (2-5)	0.3 %
2,2,4-Trimethyl-1, 3-pentanediol	1 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 31

[0178] A pigment dispersion 19 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 19, an ink composition 31 was obtained.

Pigment dispersion 19	
C.I. Pigment Blue 15:3 (average particle size: 123 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 31	
Pigment dispersion 19	33.3 %

Glycerin	3 %
1,5-Pentanediol	15 %
Compound (2-5)	0.3 %
25 % Aqueous solution of compound (13-4)	0.5 %
2,2,4-Trimethyl-1, 3-pentanediol	5 %
2-Pyrolidone	2 %
Ion-exchanged water	Balance

Example 32

[0179] A pigment dispersion 20 was prepared in the same manner as in Example 5 except that the following composition were used. Using the thus obtained pigment dispersion 20, an ink composition 32 was obtained.

Pigment dispersion 20	
C.I. Pigment Blue 56 (average particle size: 138 nm)	15 %
Formalin condensate of naphthalene sulfonate	3 %
Ion-exchanged water	Balance

Ink composition 32	
Pigment dispersion 20	33.3 %
Polyethylene glycol (molecular weight: 200)	10 %
Compound (2-4)	0.05 %
2,2,4-Trimethyl-1,3-pentanediol	4 %
Triethylene glycol monobutyl ether	2 %
Ion-exchanged water	Balance

Example 33

[0180] An ink composition 33 was prepared in the same manner as in Example 1 except that the following compositions were used.

Ink composition 33	
Carboxyl group-bonded carbon black dispersion (solid content 16.4 % by weight, average particle size 128 nm)	33.3 %

Diethylene glycol	15 %
Glycerin	5 %
Compound (2-7)	0.8 %
2,2,4-Trimethyl-1,3-pentanediol	2 %
N-methyl-2-pyrolidone	2 %
Ion-exchanged water	Balance

Example 34

[0181] An ink composition 34 was prepared in the same manner as in Example 1 except that the following compo-

sitions were used.

Ink composition 34	
Carboxyl group-bonded carbon black dispersion (solid content 16.4 % by weight, average particle size 128 nm)	33.3 %
Ethylene glycol	15 %
Compound (2-1)	1 %
2,2,4-Trimethyl-1,3-pentanediol	3 %
N-methyl-2-pyrolidone	2 %
Ion-exchanged water	Balance

Example 35

[0182] An ink composition 35 was prepared in the same manner as in Example 1 except that the following compositions were used.

Ink composition 35	
Sulfonic group-bonded carbon black dispersion (solid content 18 % by weight, average particle size 132 nm)	33 %
1,5-Pentanediol	5 %
N-methyl-2-pyrolidone	2 %
Compound (2-3)	1 %
2,2,4-Trimethyl-1,3-pentanediol	1 %
Ion-exchanged water	Balance

Example 36

[0183] An ink composition 36 was prepared in the same manner as in Example 1 except that the following compositions were used.

Ink composition 36	
Sulfonic group-bonded carbon black dispersion (solid content 18 % by weight, average particle size 132 nm)	33 %
1,5-Pentanediol	5 %
N-methyl-2-pyrolidone	2 %
Compound (2-2)	1 %
2,2,4-Trimethyl-1,3-pentanediol	1.5 %
Ion-exchanged water	Balance

Example 37

[0184] A pigment dispersion 21 was prepared in the same manner as in Example 5 except that the following compositions were used. Using the thus obtained pigment dispersion 21, an ink composition 37 was obtained.

Ink composition 21	
Carbon black (average particle size 53 nm)	15 %
Styrene-acrylate-diethanolamine methacrylate terpolymer	3 %
Ion-exchanged water	Balance

Ink composition 37	
Pigment dispersion 21	33.3 %

(continued)

Ink composition 37	
Polyethylene glycol (molecular weight: 200)	5 %
Ethylene glycol	30 %
Compound (2-5)	0.01 %
2,2,4-Trimethyl-1,3-pentanediol	8 %
Ion-exchanged water	Balance

Comparative Example 1

[0185] An ink composition 38 was prepared in the same manner as in Example 5 except that ion-exchanged water was added instead of 2,2,4-trimethyl-1,3-pentanediol in the same amount.

Comparative Example 2

[0186] An ink composition 39 was prepared in the same manner as in Example 25 except that ion-exchanged water was added instead of 2,2,4-trimethyl-1,3-pentanediol in the same amount.

Comparative Example 3

[0187] An ink composition 40 was prepared in the same manner as in Example 5 except that, instead of 2,2,4-trimethyl-1,3-pentanediol, the compound (1-1) and ion-exchanged water were added such that the content of the compound (1-1) was 2 % by weight in total.

Comparative Example 4

[0188] An ink composition 41 was prepared in the same manner as in Example 6 except that diethylene glycol monobutyl ether was added instead of 2,2,4-trimethyl-1,3-pentanediol in the same amount.

Comparative Example 5

[0189] An ink composition 42 was prepared in the same manner as in Example 10 except that diethylene glycol monobutyl ether was added instead of 2,2,4-trimethyl-1,3-pentanediol in the same amount.

Comparative Example 6

[0190] An ink composition 43 was prepared in the same manner as in Example 24 except that 2-ethyl-2-methyl-1,3-propanediol was added instead of 2,2,4-trimethyl-1,3-pentanediol in the same amount.

Comparative Example 7

[0191] An ink composition 44 was prepared in the same manner as in Example 12 except that 2-diethyl-1,3-propanediol was added instead of 2,2,4-trimethyl-1,3-pentanediol in the same amount.

Comparative Example 8

[0192] An ink composition 45 was prepared in the same manner as in Example 33 except that 1,7-heptanediol was added instead of 2,2,4-trimethyl-1,3-pentanediol and the compound (2-5) in the same amount as a total amount thereof.

Comparative Example 9

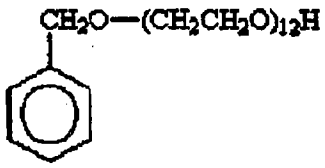
[0193] An ink composition 46 was prepared in the same manner as in Example 6 except that 1,8-octanediol was added instead of 2,2,4-trimethyl-1,3-pentanediol in the same amount.

Comparative Example 10

[0194] An ink composition 47 was prepared in the same manner as in Example 14 except that 1,7-heptanediol was added instead of 2,2,4-trimethyl-1,3-pentanediol in the same amount.

Comparative Example 11

[0195] An ink composition 48 was prepared in the same manner as in Example 4 except that 6 % by weight of the following compound (15) was added instead of the compound (1-5).

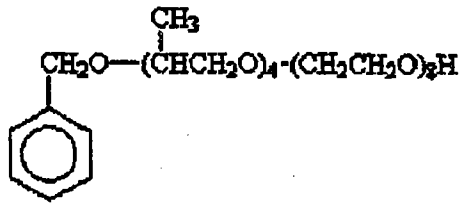


(15)

Comparative Example 12

[0196] The following ink ingredients were mixed and stirred. The mixture was adjusted to pH 8 with 10 % aqueous solution of lithium hydroxide and then filtered with a membrane filter having an average aperture size of 0.1 μm, thereby obtaining an ink composition 49.

Ink composition 49	
C.I. Acid Blue 234	2 %
Polyethylene glycol #200	10 %
Following Compound (16)	6 %
2,2,4-trimethyl-1,3-pentanediol	1 %
Ion-exchanged water	Balance



(16)

Comparative Example 13

[0197] An ink composition 50 was prepared in the same manner as in Example 5 except that ion-exchanged water was added instead of the compound (1-1), the compound (1-3), and 25 % aqueous solution of the compound (13-3) in the same amount as a total amount thereof.

Comparative Example 14

[0198] An ink composition 51 was prepared in the same manner as in Example 5 except that 2,2,4-trimethyl-1,3-pentanediol was further added instead of the compound (1-1), the compound (1-3), and 25 % aqueous solution of the compound (13-3) in the same amount as a total amount thereof.

Comparative Example 15

[0199] An ink composition 52 was prepared in the same manner as in Example 15 except that 2,2,4-trimethyl-1,3-pentanediol was further added instead of the compound (1-1) in the same amount.

<Recording apparatus>

[0200] The following tests were conducted on the inks described in Examples and Comparative Examples. The following three recording apparatuses were employed.

Recording apparatus (A)

[0201] A piezoelectric ink jet printer having a plurality of nozzles, wherein each of the nozzles is capable of ejecting ink droplets each having a volume of 23 pl at a dot density of 600 dpi at the maximum on a plain paper.

Recording apparatus (B)

[0202] A thermal ink jet printer having a plurality of nozzles, wherein each of the nozzles are capable of ejecting ink droplets each having a volume of 4 pl at a dot density of 1200 dpi at the maximum on a plain paper.

Recording apparatus (C)

[0203] A piezoelectric ink jet printer having 48 nozzles arranged at a 360 dpi pitch, wherein each of the nozzles is capable of ejecting ink droplets having a volume of 4 pl, 7 pl or 11 pl depending upon an image to be printed at a dot density of 720 dpi at the maximum on a plain paper.

[0204] The recording apparatus used for printing and the results of the evaluations are summarized in Table 1 and Table 2.

<Evaluation items>

1) Sharpness of image

[0205] Printing was conducted on a recording medium, My Paper, manufactured by NBS Ricoh Company, Ltd. (sizing degree: 12s, air-permeability; 16s). After drying, the blur, color tone, and density of the image were observed with naked eyes and measured using a spectrodensitometer (manufactured by X-Rite Co., Ltd.). The evaluation was made in a comprehensive manner.

A: Excellent
B: Good
C: Fair
D: No good

2) Drying property of image

[0206] A solid image was printed on the recording medium. On printing, a filter paper was pressed on the recording medium with a pressure of 0.1 kg/cm^2 and the time until the ink became sufficiently dry not to transfer to the filter paper was measured.

A: Not longer that 3 seconds.
B: Longer than 3 seconds and shorter than 20 seconds.
C: 20 seconds or longer.

3) Strike-through

[0207] A solid image having a density of 1.0 as measured with a spectrodensitometer (manufactured by X-Rite Co., Ltd.) was printed on the recording medium and the image was observed from the reverse side thereof with naked eyes.

A: The boundary between the solid image area and the unprinted area is completely vague so that the recording

medium can be used for double-side printing without any problem.
B: The boundary between the solid image part and the unprinted area is nearly vague so that the recording medium can be used for double-side printing without any problem.
C: The colorant was not penetrated to the reverse side of the recording medium and the boundary between the solid image area and the unprinted area is a little vague so that the recording medium can be used for double-side printing without any problem.
D: The colorant was penetrated to the reverse side of the recording medium so that the recording medium was not able to be used for double-side printing.

4) Anti-scratching property

[0208] An image printed on the recording medium using each of the inks was rubbed with a finger, a cloth, an eraser and a marking pen 30 seconds after the printing. The state of the image after the rubbing was observed with naked eyes.

A: Changes were observed.
B: No change was observed.

5) Uniformity of image

[0209] A solid image was printed on the recording medium and observed after drying.

A: The recording medium was uniformly colored with the ink as observed under magnification.
B: The recording medium was uniformly colored with the ink as observed with naked eyes.
C: The recording medium was colored with the ink so unevenly that the surface of the medium was seen in some places with naked eyes.

6) Preservability

[0210] An ink jet printer was left with an ink set therein at 60°C for 7 days. Thereafter, a conventionally known cleaning operation of the ink jet printer was conducted until the printing function of the printer was restored to normal state.

A: Restored with one cleaning operation.
B: Restored with 2 to 5 cleaning operations.
C: Not restored with 5 cleaning operations.

<Recording medium>

Example 38 to Example 57

[0211] Using the ink of Example 14, printing was performed on each of the following recording media. Then, evaluation was conducted.

Example 38

[0212] Xerox Paper R, manufactured by Xerox Corp. (sizing degree: 8s, air-permeability: 20s)

Example 39

[0213] REFEX, manufactured by Australian Paper Manufacturers Ltd. (Australia) (sizing degree: 25s, air-permeability: 4s)

Example 40

[0214] NBS Copying and Printing Paper 90K, manufactured by NBS Ricoh Company, Ltd. (sizing degree: 60s, air-permeability: 68s)

Example 41

[0215] PB Paper, manufactured by Canon Inc. (sizing degree: 21s, air-permeability: 8s)

Example 42

[0216] NBS Copying and Printing Paper 45K, manufactured by NBS Ricoh Company, Ltd. (sizing degree: 11s, air-permeability: 45s)

Example 43

[0217] Yamayuri, manufactured by Honshu Paper Co., Ltd. (sizing degree: 12s, air-permeability: 21s)

Example 44

[0218] Togen PPC Paper Type S, manufactured by Ricoh Company, Ltd. (sizing degree: 22s, air-permeability: 13s)

Example 45

[0219] Xerox Paper P, manufactured by Xerox Corp. (sizing degree: 24s, air-permeability: 19s)

Example 46

[0220] Multiace, manufactured by Xerox Corp. (sizing degree: 25s, air-permeability: 17s)

Example 47

[0221] Xerox 4024 Paper, manufactured by Xerox Corp. (sizing degree: 32s, air-permeability: 21s)

[0222] Using the ink of Example 24, printing was conducted on each of the following recording media. Then, evaluation was conducted.

Example 48

[0223] Xerox Paper R, manufactured by Xerox Corp. (sizing degree: 8s, air-permeability: 20s)

Example 49

[0224] REFEX, manufactured by Australian Paper Manufacturers Ltd. (Australia) (sizing degree: 25s, air-permeability: 4s)

Example 50

[0225] NBS Copying and Printing Paper 90K, manufactured by NBS Ricoh Company Ltd. (sizing degree: 60s, air-permeability: 68s)

Example 51

[0226] PB Paper, manufactured by Canon Inc. (sizing degree: 21s, air-permeability: 8s)

Example 52

[0227] NBS Copying and Printing Paper 45K, manufactured by NBS Ricoh Company Ltd. (sizing degree: 11s, air-permeability: 45s)

Example 53

[0228] Yamayuri, manufactured by Honshu Paper Co., Ltd. (sizing degree: 12s, air-permeability: 21s)

Example 54

[0229] Togen PPC Paper Type S, manufactured by Ricoh Company Ltd. (sizing degree: 22s, air-permeability: 13s)

Example 55

[0230] Paper P, manufactured by Xerox Corp. (sizing degree: 24s, air-permeability: 19s)

Example 56

[0231] Multiace, manufactured by Xerox Corp. (sizing degree: 25s, air-permeability: 17s)

Example 57

[0232] Xerox Paper 4024, manufactured by Xerox Corp. (sizing degree: 32s, air-permeability: 21s)

[Table 1]

	Device	1)	2)	3)	4)	5)	6)
Example 1	B	B	A	C	A	A	A
2	C	B	A	C	A	A	A
3	A	B	A	C	A	A	A
4	B	B	A	C	A	A	A
5	A	A	A	A	A	A	A
6	C	A	A	A	A	A	A
7	A	B	A	B	B	B	A
8	C	A	A	A	A	A	A
9	B	B	A	B	B	B	A
10	A	A	A	A	A	A	A
11	B	B	A	B	A	A	A
12	C	A	A	A	A	A	A
13	B	B	A	B	B	B	A
14	C	A	A	A	B	B	A
15	A	A	A	A	A	A	A
16	B	B	A	B	B	B	A
17	A	A	A	A	A	A	A
18	C	A	A	B	B	B	A
19	A	A	A	A	B	B	A
20	C	B	A	C	A	A	A
21	B	B	A	C	A	A	A
22	A	B	A	C	A	A	A
23	B	B	A	C	A	A	A

1) Sharpness of image
2) Drying property of image
3) Strike-through
4) Anti-scratching property
5) Uniformity of image
6) Preservability

[Table 1] (continued)

	Device	1)	2)	3)	4)	5)	6)
24	C	A	A	A	A	A	A
25	B	A	A	A	A	A	A
26	C	B	A	B	B	B	A
27	A	A	A	A	A	A	A
28	B	B	A	B	B	B	A
29	A	A	A	A	A	A	A
30	C	B	A	B	A	A	A
31	A	A	A	A	A	A	A
32	C	B	A	B	B	B	A
33	B	A	A	A	B	B	A
34	A	A	A	A	A	A	A
35	B	B	A	B	B	B	A
36	C	A	A	A	A	A	A
37	B	A	A	A	B	B	A

1) Sharpness of image
2) Drying property of image
3) Strike-through
4) Anti-scratching property
5) Uniformity of image
6) Preservability

[Table 2]

	Device	1)	2)	3)	4)	5)	6)
Comp. Ex. 1		D	C	A	D	D	A
2		D	C	A	D	D	A
3		B	B	D	B	C	C
4		C	A	D	D	C	B
5		C	B	C	D	C	B
6		D	C	A	D	D	A
7		D	C	A	D	D	A
8		D	C	A	D	D	A
9		D	C	A	D	D	A
10		D	C	A	D	D	A
11		D	C	A	D	D	A
12		D	C	A	D	D	A

1) Sharpness of image
2) Drying property of image
3) Strike-through
4) Anti-scratching property
5) Uniformity of image
6) Preservability

[Table 2] (continued)

	Device	1)	2)	3)	4)	5)	6)
13		B	C	A	D	D	A
14		B	B	B	C	D	C
15		B	B	B	C	D	B
Example 38	C	B	A	B	B	B	-
39	C	B	A	B	B	B	-
40	C	B	A	A	B	B	-
41	C	B	A	A	B	A	-
42	C	B	A	A	B	A	-
43	C	B	A	A	B	B	-
44	C	B	A	A	B	A	-
45	C	B	A	A	B	B	-
46	C	B	A	A	B	A	-
47	C	B	A	A	B	A	-
48	C	B	A	B	B	B	-
49	C	B	A	B	B	B	-
50	C	B	A	A	B	B	-
51	C	B	A	A	B	A	-
52	C	B	A	A	B	A	-
53	C	B	A	A	B	B	-
54	C	B	A	A	B	A	-
55	C	B	A	A	B	A	-
56	C	B	A	A	B	A	-
57	C	B	A	A	B	A	-

1) Sharpness of image
2) Drying property of image
3) Strike-through
4) Anti-scratching property
5) Uniformity of image
6) Preservability

[0233] According to the present invention, there can be provided an aqueous recording liquid which exhibits high penetrability and high drying property irrespective of the type of a colorant and a paper and which allows production of an image of improved quality with little blur. Also, the recording liquid has neither phase separation, aggregation nor increase in viscosity and thus suitable for a recording method in which an image is formed on a recording medium by ejecting and jetting a recording liquid as droplets onto the recording medium from a minute ejection nozzle.

[0234] There can be also provided a recording liquid cartridge containing the aqueous recording liquid which has high penetrability, high reliability and high safety and which allows printing of image with excellent properties, and a recording apparatus including the cartridge.

Claims

1. An aqueous recording liquid comprising a colorant, 2,2,4-trimethyl-1,3-pentanediol, and at least one surfactant

selected from the group consisting of polyoxyethylene alkyl ethers and polyoxyethylene alkyl ether acetates.

2. An aqueous recording liquid as claimed in claim 1, wherein said polyoxyethylene alkyl ethers are represented by the general formula (1);

$$R_1O(CH_2CH_2O)_pH \quad (1)$$

wherein R_1 represents a straight or branched alkyl group having 8 to 14 carbon atoms and p represents an integer of 1 to 30.

3. An aqueous recording liquid as claimed in claim 1 or 2, wherein said polyoxyethylene alkyl ether acetates are represented by the general formula (2);

$$R_2O(CH_2CH_2O)_qCH_2COOM \quad (2)$$

wherein R_2 represents a straight or branched alkyl group having 8 to 14 carbon atoms, q represents an integer of 3 to 8, and M represents an alkali metal ion, a quaternary ammonium, a quaternary phosphonium or an alkanolamine.

4. An aqueous recording liquid as claimed in any one of claims 1-3, wherein said 2,2,4-trimethyl-1,3-pentanediol is present in an amount of not less than 0.1 % by weight but not greater than 8 % by weight.

5. An aqueous recording liquid as claimed in any preceding claim, wherein said surfactant is present in an amount of not less than 0.01 % by weight but not greater than 4 % by weight.

6. An aqueous recording liquid as claimed in any preceding claim, wherein said 2,2,4-trimethyl-1,3-pentanediol is present in an amount of not less than 0.1 % by weight but not greater than 8 % by weight and said surfactant is present in an amount of not less than 0.01 % by weight but not greater than 4 % by weight.

7. An aqueous recording liquid as claimed in any preceding claim, further comprising at least one water-soluble organic solvent selected from the group consisting of glycerin, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, 1,5-pentanediol, tetraethylene glycol, 1,6-hexanediol, 2-methyl-2,4-pentanediol, polyethylene glycol, 1,2,4-butanetriol, 1,2,6- hexanetriol, thiodiglycol, 2-pyrolidone, N-methyl-2-pyrolidone, N-hydroxyethyl-2-pyrolidone and 1,3-dimethyl-2-imidazolidinone.

8. An aqueous recording liquid as claimed in any preceding claim, wherein said colorant is a pigment.

9. An aqueous recording liquid as claimed in claim 8, wherein said pigment has an average particle size in the range of 10 to 200 nm.

10. An aqueous recording liquid as claimed in claim 8 or 9, further comprising a dispersant having a carboxyl group, so that dispersion of said pigment in water is stabilized.

11. An aqueous recording liquid as claimed in any one of claims 8-10, wherein said pigment is modified to have a hydrophilic group, so that dispersion of said pigment in water is stabilized.

12. An aqueous recording liquid as claimed in claim 11, wherein said hydrophilic group bonded to said pigment is a carboxyl group.

13. A recording method for forming an image on a recording medium, comprising ejecting an aqueous recording liquid according to any preceding claim as droplets onto said recording medium from a minute ejection nozzle.

14. A recording method as claimed in claims 13, wherein said aqueous recording liquid ejected by being applied with thermal energy.

15. A recording method as claimed in claim 13 or 14, wherein said recording medium is formed of pulp fibers and has a sizing degree of at least 10 seconds and an air-permeability of 5 to 50 seconds.

16. A recording method as claimed in any one of claims 13-15, wherein each of said droplets of the aqueous recording liquid ejected from said ejection nozzle has an ejection volume V (in pl) satisfying the following equation:

$$2.5 \times 10^8/R^{2.6} \leq V \leq 6.0 \times 10^8/R^{2.6}$$

wherein R represents the maximum recording density (in dpi) at which said droplets are ejected on said recording medium formed of pulp fibers and having a sizing degree of at least 10 seconds and an air-permeability of 5 to 50 seconds.

17. A recording method as claimed in any one of claims 13-16, wherein a plurality droplets of said aqueous recording liquid are successively ejected from one ejection nozzle or separate ejection nozzles to form an image on the recording medium such that at least a part of pixels of the droplets are overlapped, and wherein two of aqueous recording liquid droplets which form the partially overlapped pixels are ejected with a time difference of not greater than 0.125 ms.

18. A recording liquid cartridge having a recording liquid container containing an aqueous recording liquid according to any one of claims 1-12.

19. A recording liquid cartridge as claimed in claim 18, further comprising a recording head for ejecting droplets of an aqueous recording liquid according to any one of claims 1-12.

20. An ink jet recording device comprising a recording liquid cartridge according to claim 19.

FIG. 1

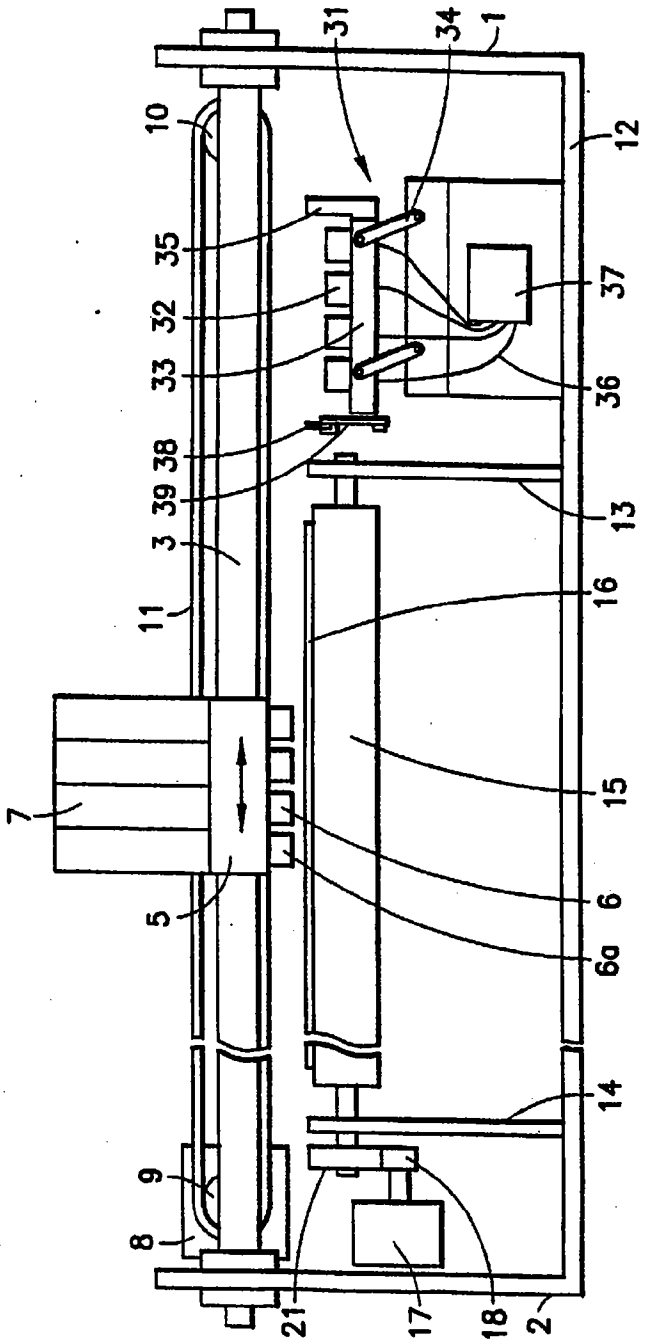


FIG. 2

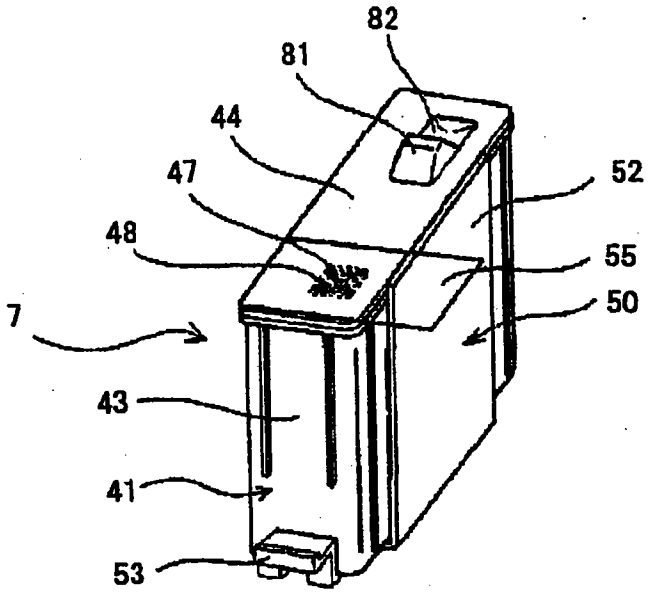

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FIG. 3

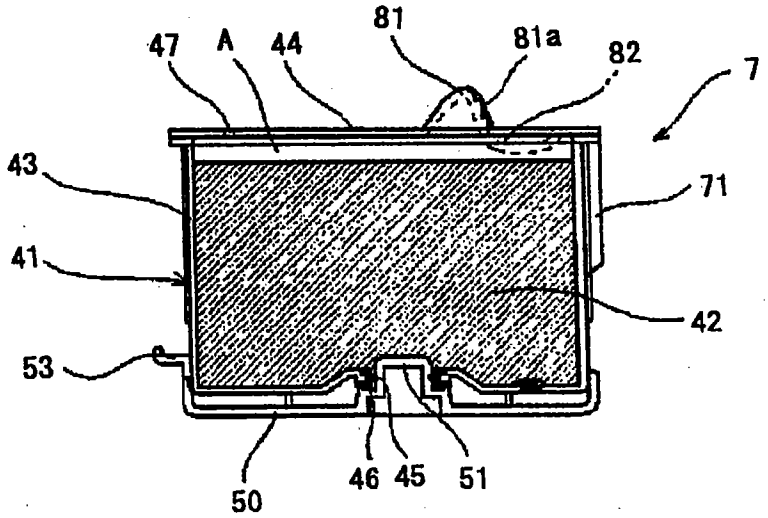
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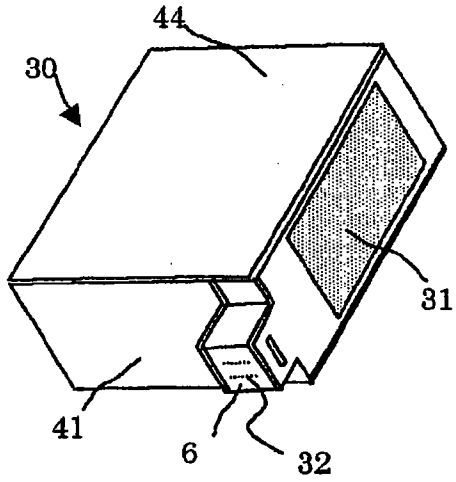
FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
EP 02 00 6495

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	EP 0 812 888 A (SEIKO EPSON CORP) 17 December 1997 (1997-12-17) * page 6, line 49; claims 1,7 *	1-20	C09D11/00
Y	DATABASE WPI Section Ch, Week 199816 Derwent Publications Ltd., London, GB; Class A25, AN 1998-175178 XP002199227 & JP 10 036733 A (RICOH KK), 10 February 1998 (1998-02-10) * abstract *	1-20	
A	DATABASE WPI Section Ch, Week 199702 Derwent Publications Ltd., London, GB; Class A97, AN 1997-017646 XP002199228 & JP 08 283640 A (RICOH KK), 29 October 1996 (1996-10-29) * abstract *	1-20	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	US 5 992 117 A (SCHMIDT GEORGE A) 30 November 1999 (1999-11-30) * claim 12 *	1-20	C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	17 May 2002	Ellrich, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 02 00 6495

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17-05-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0812888 A	17-12-1997	DE 69706602 D1	18-10-2001
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(54) Inkjet ink

(57) The inks provide excellent ink-jet prints having excellent colour and performance attributes. The aqueous inks each comprise a colourant (CMYK), a long chain first surfactant and a second short-chain surfactant.

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Description

[0001] The present invention generally relates to an ink-jet ink and to a method of printing therewith, and in particular to a specific ink formulation for colour and performance attributes. This ink formulation also provides for improved ink-jet print quality.

[0002] Ink-jet printing is a non-impact printing process in which droplets of ink are deposited on a print medium in a particular order to form alphanumeric characters, area-fills, and other patterns thereon. Low cost and high quality of the hardcopy output, combined with relatively noise-free operation, have made ink-jet printers a popular alternative to other types of printers used with computers. Notwithstanding their recent success, intensive research and development efforts continue toward improving ink-jet print quality. A surge in interest in ink-jet printing especially in the area of photographic printing has resulted in the need to produce high quality prints at a reasonable cost. The challenge remains to further improve the print quality of ink-jet prints. The emerging use of ink-jet prints for digital photos, requires high-resolution images that have accurate color, are durable, and do not show banding of colors.

[0003] Color ink-jet printers, such as a DesignJet® printer available from Hewlett-Packard Company, typically use three inks of differing hues: magenta, yellow, and cyan, and optionally black. The particular set of colorants, e.g., dyes, used to make the inks is called a "primary dye set." A spectrum of colors, e.g., secondary colors, can be generated using different combinations of the primary dye set.

[0004] In general, a successful ink set for color ink-jet printing must be compatible with the ink-jet pen and the printing system. Some of the required properties for the ink-jet ink include color attributes, such as mottle, coalescence, and saturation.

[0005] "Mottle" and "coalescence" are defined as inconsistencies (or incongruities) of print density with the same print block due to printing defects and solvent/ink interactions with the media. Good color saturation is attained by maximizing the depth and shade of colors, which is also affected by ink/media interactions.

[0006] Inks are known which possess one or more of the foregoing properties. However, few inks are known that possess all the foregoing properties, since an improvement in one property often results in the degradation of another property. Thus, many inks used commercially represent a compromise in an attempt to achieve an ink evidencing at least an adequate response in each of the foregoing considerations. Thus, there remains a need in the art to further improve the color quality of the ink-jet prints without sacrificing pen performance and reliability and wherein the complexity of printer and software design is reduced.

[0007] In accordance with the invention, inks suitable for use in ink-jet inks and method for formulating the same are provided. It has been found that a synergy which leads to distinct improvements in coalescence, mottle, color saturation and can be produced by the combination of certain colorants, surfactants, and second or co-surfactants, defined as compounds containing from about 6 to about 10 carbons that is soluble in water by at least 3% by weight. This combination provides a basis for an ink formulation that provides for good color and performance attributes.

[0008] Finding a relationship amongst surfactant choices allows a much larger formulation space for future products. Surprisingly, the synergy present amongst the selected surfactants results in a very stable formulation that allows the formulator to significantly increase the choices of suitable surfactants and solvents for use. Moreover, without limitation to theory, it is believed the combination of the surfactants second surfactant increases the solubility of the ink components in the micelles formed by the use of these surfactants. This leads to deeper color saturation and much less mottle and coalescence than with either component alone. This formulation works well on any plain paper media special media.

[0009] In the practice of this invention, yellow, cyan, magenta and black aqueous inks each comprise from about 0.1 to about 20 wt % of at least one colorant in the ink formulations; from about 5 to about 15 wt % of at least one linear, branched, or aromatic short chain second or co-surfactant containing from about 6 to about 10 carbons and being soluble in water by at least about 3% by weight, and from about 0.2 to about 6 wt % of at least one linear, branched or unbranched nonionic, anionic, cationic, or zwitterionic first surfactant containing from about 8 to about 18 carbons, preferably from about 11 about 18 carbons. The co-surfactant my be of any charge. Additionally other independently selected ingredients can be added including those from the group consisting of buffers, biocides, and metal chelators; and the balance water. Of course, a person skilled in the art of ink formulation would optimize the ink by coordinating the charges of the various ingredients in the final formula.

While the specification concludes with claims particularly pointing out and distinctly claiming that which is regarded as the present invention, a number of preferred embodiments of this invention can be more readily ascertained from the following description of the invention.

[0010] All concentrations herein are in weight percent of total ink composition unless otherwise indicated. The purity of all components is that employed in normal commercial practice for ink-jet inks.

Colorants

[0011] In the practice of this invention, yellow, cyan, magenta, and black aqueous inks each comprise from about

0.1 to about 20 wt % of at least one colorant. If used herein, the preferable amount of cationic dye is from about 0.1 to about 10 wt%; from about 0.1 to about 10 wt% of pigment; and from about 1 to about 20 wt % of at least one black colorant in black ink formulations. The black ink can also be a composite of the three primary colors, yellow, cyan, and magenta.

[0012] Dyes - Dyes, whether water-soluble or water-insoluble, may be employed in the practice of the present invention. Examples of water-soluble dyes include the sulfonate and carboxylate dyes, specifically, those that are commonly employed in ink-jet printing. Specific examples include: Sulforhodamine B (sulfonate), Acid Blue 113 (sulfonate), Acid Blue 29 (sulfonate), Acid Red 4 (sulfonate), Rose Bengal (carboxylate), Acid Yellow 17 (sulfonate), Acid Yellow 29 (sulfonate), Acid Yellow 42 (sulfonate), Acridine Yellow G (sulfonate), Nitro Blue Tetrazolium Chloride Monohydrate or Nitro BT, Rhodamine 6G, Rhodamine 123, Rhodamine B, Rhodamine B Isocyanate, Safranine O, Azure B, Azure B Eosinate, Basic Blue 47, Basic Blue 66, Thioflacin T (Basic Yellow 1), and Auramine O (Basic Yellow 2), all available from Aldrich Chemical Company. Examples of water-insoluble dyes include azo, xanthene, methine, polymethine, and anthroquinone dyes. Specific examples of pigmentsinclude Ciba-Geigy Orasol Blue GN, Ciba-Geigy Orasol Pink, and Ciba-Geigy Orasol Yellow. Any dye available and compatible with the other formulated ingredients of this invention may be used as colorants.

Vehicle

[0013] The inks of the present invention comprise an aqueous vehicle comprising the following components (in wt % of total ink composition): from about 5 to about 15, preferably from about 7 to about 11, wt % of at least one second surfactant. The surfactant of the invention is present in an amount of from about 0.2 to about 6, preferably from about 0.5 to about 3 wt % of the ink formula. Because of solubility limitations, the more preferred surfactants have about 8 to 18 carbons. A preferred surfactant is an ethylene oxide surfactant. Additionally other independently selected ingredients can be added, each in an amount ranging of up to 3% (from 0 to about 3%) by wt, including those from the group consisting of buffers, biocides, and metal chelators; and the balance water.

[0014] Buffer: The inks of the present invention optionally comprise 0 to about 3 wt % buffer. More preferably, the inks comprise from about 0.1 to about 0.5 wt % buffer, with a concentration from about 0.1 to about 0.3 wt % being the most preferred.

[0015] Buffers employed in the practice of the invention to modulate pH can be organic-based biological buffers or inorganic buffers, preferably, organic-based. Further, the buffers employed should maintain a pH ranging from about 3 to about 9 in the practice of the invention, preferably about 6.5 to about 8.5 and most preferably from about 7.2 to 8.5. Examples of preferably-employed buffers include Trizma Base, available from companies such as Aldrich Chemical (Milwaukee, Wis.), 4-morpholineethanesulfonic acid (MES), b-hydroxy-4-morpholinepropanesulfonic acid (MOPSO), and 4-morpholinepropanesulfonic acid (MOPS). Most preferably, TRIZMA is employed in the practice of the invention.

[0016] Metal Chelator: The inks of the present invention optionally comprise 0 to about 3 wt % metal chelator. More preferably, the inks comprise from about 0.1 to about 0.5 wt % metal chelator, with a concentration from about 0.1 to about 0.3 wt % being the most preferred.

[0017] Metal chelators employed in the practice of the invention are used to bind metal cations that may be present in the ink. Examples of preferably-employed metal chelators include: Ethylenediaminetetraacetic acid (EDTA), Diethylenetriaminepentaacetic acid (DTPA), trans-1,2-diaminocyclohexanetetraacetic acid (CDTA), (ethylenedioxy) diethylenedinitrilotetraacetic acid (EGTA), or other chelators that can bind metal cations. More preferably, EDTA, and DTPA; and most preferably EDTA in its disodium salt form is employed in the practice of the invention.

[0018] Biocide: The inks of the present invention optionally comprise 0 to about 3 wt % biocide. More preferably, the inks comprise from about 0.1 to about 0.5 wt % biocide, with a concentration from about 0.1 to about 0.3 wt % being the most preferred.

[0019] Any of the biocides commonly employed in ink-jet inks may be employed in the practice of the invention, such as Nuosept 95, available from Huls America (Piscataway, N.J.); Proxel GXL, available from Zeneca (Wilmington, Del.); and glutaraldehyde, available from Union Carbide Company (Bound Brook, N.J.) under the trade designation Ucarcide 250. Proxel GXL is the preferred biocide.

The specific ink set disclosed herein is expected to find commercial use in ink-jet color printing.

EXAMPLES

[0020] Inks are formulated and different properties of the formulated inks are measured in an effort to assess the benefits attained in the practice of the invention, namely, mottle and coalescence, which are inconsistencies (or incongruities) of print density with the same print block due to printing inconsistencies and solvent/ink interactions with the media. Good saturation is attained by maximizing the depth and shade of colors, which is affected by ink/media interactions.

Table 1

Ink ID	Dye	Co surfactant	Surfactant	Media	Saturation
1-1	Cyan	1,2-hexanediol	Linear, nonionic	HP Bright White	Excellent
1-2	Magenta	2,2-diethyl-1,3-propanediol	Linear, nonionic	HP Bright White	Excellent
1-3	Magenta	2,2-diethyl-1,3-propanediol	Branch, nonionic	HP Bright White	Excellent
1-4	Magenta	2,2-diethyl-1,3-propanediol	Linear, nonionic	HP Premium Plus Photo Paper, Glossy	Excellent
1-5	Yellow	2-methyl-2-propyl-1,3-propanediol	Linear, nonionic	HP Premium Plus Photo Paper, Glossy	Excellent
1-6	Cyan	1,2-hexanediol	Aromatic nonionic	HP Premium Plus Photo Paper, Glossy	Excellent
1-7	Magenta	1,2-hexanediol	Anionic	HP Bright White	Excellent
1-8	Yellow	1,2-hexanediol	Zwitterionic	HP Bright White	Excellent
1-9	Magenta	1,2-hexanediol	Branched, aromatic, nonionic	HP Bright White	Excellent
1-10	Magenta	1,2-hexanediol	Zwitterionic	HP Bright White	Excellent
1-11	Cyan	1,2-propanediol	Branch, nonionic	HP Bright White	Poor
1-12	Magenta	2-methyl-1,3-methanediol	Linear, nonionic	HP Bright White	Good
1-13	Magenta	Trimethylol-propane	Branch, nonionic	HP Premium Plus Photo Paper, Glossy	Poor
1-14	Yellow	Glycerol	Branch, nonionic	HP Bright White	Poor

[0021] Examples 1-1 to 1-10 contain the co-surfactants of this invention and show excellent saturation. Examples 1-11 to 1-14 do not contain the specific combinations disclosed herein and show poorer results.

Claims

1. An inkjet ink comprising a colorant, a first surfactant containing from 8 to 18 carbons, and a second surfactant containing from 6 to 10 carbons and wherein said second surfactant is soluble in water by at least 3% by weight.

2. An inkjet ink as claimed in Claim 1, wherein said colourant is anionic, said first surfactant is anionic and is present in an amount from 0.2% to 6% by wt and said second surfactant is anionic.

3. An inkjet ink as claimed in claim 1 or 2 comprising from 0.1% to 20% by wt of said colorant, from 0.2% to 6% by wt of said first surfactant, and from 5% to 15% by wt of said second surfactant.

4. An inkjet ink as claimed in claim 1 wherein said colourant is cationic.

5. An inkjet ink as claimed in Claim 4 comprising from 0.1% to 10% by wt of said cationic colorant, from 0.2% to 6% by wt of said first surfactant, and from 5% to 15% by wt of said second surfactant.

6. An inkjet ink as claimed in any preceding claim additionally comprising from 0% to 3% of at least one of a buffer, a biocide, a metal chelator or other non-surfactant solvents.

7. An inkjet ink as claimed in any preceding claim wherein said colorant is a pigment.

8. An inkjet ink as claimed in any of claims 1 to 6 wherein said colorant is a dye.

9. An inkjet ink as claimed in any preceding claim wherein said second surfactant is 1,2-hexanediol; 2,2-diethyl-1,3-propanediol; 2-methyl-2-propyl-1,3-propanediol; or any mixtures thereof.

10. A method of printing with an inkjet ink printer displaying improved print attributes comprising employing an inkjet ink as claimed in any preceding claim.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 25 4522

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C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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Y : particularly relevant if combined with another document of the same category
A : technological background
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E : earlier patent document, but published on, or after the filing date
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(54) Ink, and a color ink-jet recording method using the same

(57) Provided is an ink, having a surface tension of not less than 30 mN/m and a viscosity of not more than 5 mPa • s, and comprising a water-soluble dye, water, at least one compound selected from the Compound Groups A and B, and at least one compound selected from the Compound Group C.

EP 0 769 536 A2

Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an ink composition (hereafter referred to simply "ink") which can achieve both high-precise color images and reliability, and to a color ink-jet recording method for conducting a recording making use of the aforementioned ink.

Related Background Art

In recent years, the aspects of lowering running costs in ink-jet printers and also reducing an amount of a refuse produced thereby have called for a type of recording apparatus in which an ink tank is set separate from a printing head, so that the ink tank alone can be replaced. Such apparatus have already been utilized to a certain extent.

However, It has been found that, in a recording apparatus in which only an ink tank is replaced, there may happen a case that problems may occur as follows: Namely, air exists there in nozzles and ink passages of the ink tank when it is replaced. And therefore, there may occur an inconvenience that such air may remain in the tank, in the form of bubbles, when a new ink is set thereto. Particularly, with ink-jet recording systems which use pressure pulses as the force for forming droplets, the bubbles which remain fixed within the ink will cause serious problems on a subsequent droplet formation.

Moreover, development of high-density printing heads for color ink-jet recording apparatus has progressed so that devices capable of high-quality printing become to have been prepared. However, there are problems with the ink to be used in such devices, since increasingly smaller droplets of ink (in a range of 3 to 50 picoliters per droplet) must be ejected in a stable and controlled manner at high frequencies, in order to conduct high-quality recording, which presents a problem in dynamics. Further, there is a problem with the reliability of such ink, as the ink must not plug up nozzles, nor remain as a residue on a surface of nozzles, and must be able to be controlled at an increasingly higher level in the apparatus.

Solving such problems can never be hoped for if ink material development is only conducted as an extension of past ink material design, while the devices themselves are being designed and provided with functions for high-quality recording. It is necessary to combine various constituent materials having various functions, in a highly skilled manner, in order to provide for an ink which satisfies the various properties required therefor. Specifically, selection and combination of various materials such as substances for protecting nozzles from clogging by an ink (evaporation prevention), solvents for maintaining an ink at low viscosity and for maintaining a long term stability of solution, solvents capable of dissolving dyes in the ink, anti-foaming agents, and the like, are extremely important.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide an ink which does not easily allow for trouble within a color ink-jet recording apparatus such as a foaming-up of ink or an air inclusion in the ink, and therefore, to provide an ink which can be supplied stably to nozzles, further which has a good balance between penetration into the recording paper and feathering, which has stable ejection properties so as to allow to form stably a formation of droplets even when dealing with a small droplet formation, moreover which does not easily cause clogging of nozzles, and thus which is capable of performing a high-quality recording.

Another object of the present invention is to provide a color ink-jet recording method which is not only capable of providing high-quality color images, but also has excellent reliability.

The objects of the present invention can be achieved by the present invention. According to the present invention there is provided an ink, having a surface tension of not less than 30 mN/m and a viscosity of not more than 5 mPa • s, and comprising a water-soluble dye, water, at least one compound selected from the Compound Groups A and B, and at least one compound selected from the Compound Group C:

Compound Group A:

A-1: Ethylene glycol mono-n-butyl ether (adhesive tension: -34.3),
A-2: Ethylene glycol monophenyl ether (adhesive tension: -31.9),
A-3: Ethylene glycol monoisobutyl ether (adhesive tension: -32.5),
A-4: Diethylene glycol mono-n-butyl ether (adhesive tension: -32.3),
A-5: Diethylene glycol monohexyl ether (adhesive tension: -31.7),
A-6: Diethylene glycol monoisobutyl ether (adhesive tension: -32.5),

A-7: Triethylene glycol n-butyl ether (adhesive tension: -24.5),

A-8: Dipropylene glycol monopropyl ether (adhesive tension: -24.0), and

A-9: Ethylene oxide adduct of benzyl alcohol (adhesive tension: -20.0).

Adhesive tension measured in units of mN/m.

Data of the adhesive tensions of the compounds of Compound Group A measured by a dynamic wettability tester are shown above. The adhesive tension has the same meanings as the dynamic contact angle of contact. These figures represent an adhesive tension 5 seconds after the test mixture of 10 % by weight of a glycol ether among the compounds of Compound Group A at 10% by weight, 0.5 % by weight of a dye added only for discrimination and a balance of water is contact with paper for PPC under ordinary temperature and humidity. The greater the negative value, the greater the wettability is in a short time.

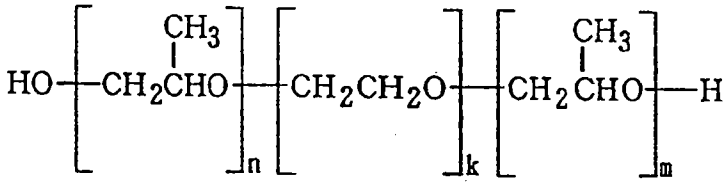
Compound Group B:

B-1: Surface active agent of ethylene oxide adduct of acetylene glycol-type,

B-2: Surface active agent of ethylene oxide - propylene oxide - ethylene oxide-type, and

B-3: Ethylene oxide adduct of higher alcohol. Compound Group C:

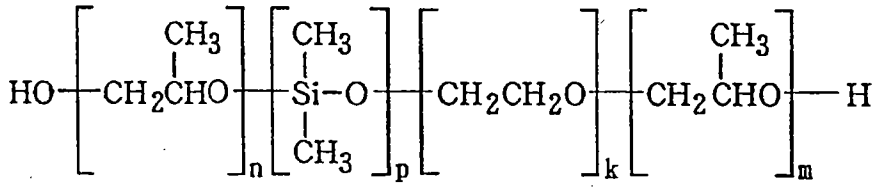
C-1: A compound represented by the formula



C − 1

wherein k is an integer of 3 to 50, m is an integer of 3 to 25, n is an integer of 3 to 25, and n + m is an integer of 6 to 50, and

C-2: A compound represented by the formula



C − 2

wherein k is an integer of 20 to 50, m is an integer of 10 to 25, n is an integer of 10 to 25, n + m is an integer of 20 to 50, and p is an integer of 2 to 5.

According to the present invention there is also provided a color ink-jet recording method for conducting a color recording using the aforementioned ink.

According to the present invention, there is provided an ink which does not easily allow for trouble within a color ink-jet recording apparatus such as a foaming-up of ink or an air inclusion in the ink, and therefore, to provide an ink which can be supplied stably to nozzles, further which has a good balance between penetration into the recording paper and feathering, which has stable ejection properties so as to allow to form stably a formation of droplets even when dealing with a small droplet formation, moreover which does not easily cause clogging of nozzles, and thus which is capable of performing a high-quality recording, as well as a color ink-jet recording method which is not only capable of providing high-quality color images, but also has excellent reliability.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A further and more detailed description of the present invention will now be given with reference to embodiments thereof. The ink of the present invention comprises, compositionally, a water-soluble dye, water, at least one compound selected from the aforementioned Compound Group A and Compound Group B, and at least one compound selected from the aforementioned Compound Group C, and, physically, has a surface tension of not less than 30 mN/m and a

viscosity of not more than 5 mPa · s. Now, the main characteristic components of the present invention will be described below.

1. Compound Group A:

A compound belonging to Compound Group A has a high compatibility with water, and a solution containing the compound of 6% by weight or more has a quick penetration which meets a color recording, is low in volatility and low in viscosity, has a high flash point, and is good in a dye solubility as well. However, if the compound is contained more than 20% by weight in the ink, an undesirable marked seepage of the ink will result to a reverse side of the paper, when paper is used as a recording medium. A necessary and sufficient amount of the compound in Compound Group A in the present invention is within the range of from 6 to 12 % by weight in the total weight of the ink.

The compounds belonging to Compound Group A have alkyl groups connected via ether bonds on the ends of the molecules, and are substances which maintain a certain level of hydrophobic properties with decreasing of viscosity and also have surfactant properties while being solvents. This is the reason why such substances are appropriate for a quick permeation of ink.

The present inventors have found that desirable properties for the inks of the present invention can be obtained when a substance exhibiting an adhesive tension of not more than -20 mN/m is used under these measurement conditions.

2. Compound Group B

(1) B-1: Ethylene oxide adduct of acetylene glycol

The substance used here is an compound in which ethylene oxide of 3.5 to 20 mol in average is added to 1 mol of acetylene glycol. Commercially available compounds include: SURFINOL 440 (3.5 mol added), SURFINOL 465 (10 mol added) (both trade name, available from NISSHIN KAGAKU CO., LTD.), ACETYNOL EH (10 mol added) (trade name, manufactured by KAWAKEN FINE CHEMICAL CO., LTD.), and the like. Also, 5 mol, 15 mol, and 20 mol adducts are capable of providing a high degree of penetration.

(2) B-2: Surface active agent of ethylene oxide - propylene oxide - ethylene oxide-type

These are known as nonionic surface active agents. Of these, strongly hydrophobic substances with an HLB range of from 4 to 8 are preferably used in the present invention.

(3) B-3: Ethylene oxide adduct of higher alcohol

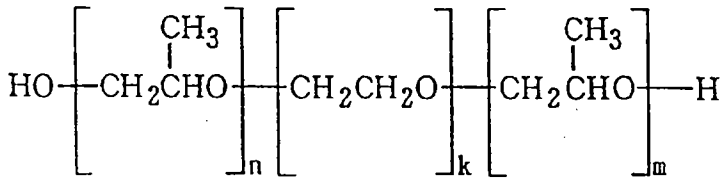
These are known as nonionic surface active agents. Of these, strongly hydrophobic substances with an HLB range of from 4 to 8 are preferably used in the present invention.

Quick penetration of ink to plain paper can be obtained by using any one of substances selected from the group consisting of the above B-1, B-2 and B-3 above in the ink of the present invention in an amount of from 0.3 to 3.0% by weight, or preferably, from 0.5 to 1.0% by weight.

3. Compound Group C

The compounds of Compound Group C do not have so high compatibility with water, but have a function to provide the ink with a foaming-resistant property and a foam-removing property. These compounds are particularly preferably used concurrently with a compound of Compound Group A. That is because the substances of Compound Group A increase the solubility of the substances of Compound Group C, thereby efficiently manifesting the foaming-resistant functions thereof.

(1) The compound C-1 is of the general formula

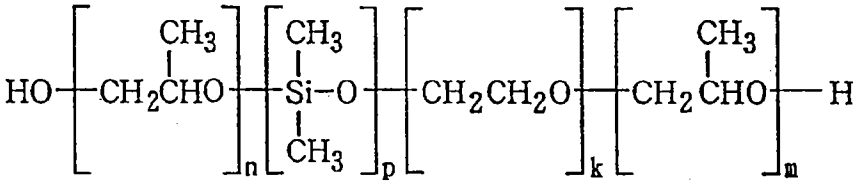


the structural feature of which is that at both ends of the molecule propylene glycol is bonded, and the middle portion of the molecule is of an ethylene glycol structure. Due to such a structure, this compound is considered to maintain a certain level of hydrophobic property within an aqueous medium, while the hydrophobic atom groups (propylene glycol) at both ends decrease a surface tension of the aqueous medium, thereby providing an ink with a foaming-resistant property.

As to silicone-type foam-removing agents which have silicone structures at the end of the molecule, there have been developed many substances, but these become emulsified and dispersed in an aqueous medium, and become inhomogeneous. While such silicone-type foam-removing agents have excellent properties as a foam-removing agent, the long-term stability thereof is poor, the surface tension reaches a value of 30 mN/m or lower so that it is difficult to form droplets, and low in the meniscus maintainability. Thus, it is inappropriate for a foam-removing agent.

A preferable compound regarding the substance in the aforementioned formula C-1 is such with HLB in the range of 4 to 10, a liquid oligomer with a molecular weight in the range of 400 to 5,000, wherein k is 3 to 50, m is 3 to 25, n is 3 to 25, and n + m is 6 to 50.

(2) The compound C-2 is of the general formula



The Compound C-2 in the above formula is a substance having alkyl silicone diol units so as to increase the foaming-resistant and foam-removing properties as compared to that of C-1, with an HLB value in a range of from 4 to 10, being a liquid oligomer with a molecular weight in a range of from 400 to 5,000, wherein k is an integer of 20 to 50, m is an integer of 10 to 25, n is an integer of 10 to 25, n + m is an integer of 20 to 50, and p is an integer of 2 to 5.

In the ink of the present invention, either C-1 or C-2 is used in an amount, generally, within a range of 0.5 to 5.0% by weight, and more preferably 1.1 to 2.0% by weight, although it differs depending on the ink media employed. A specific amount of the compound to be added differs depending on the ink media employed, but should be added within a compatible range.

The compounds in Compound Group C exhibit a surface active property in the ink of the present invention, and the foaming-resistant and foam-removing properties thereof allow to form stable droplets and to reduce an air inclusion at the time of filling ink. A characteristic point thereof is that the compound belonging to the Compound Group C is completely dissolved in the ink, so that the surface tension of the ink is not dramatically reduced, and that surface tension of not less than 30 mN/m, which is one of requirements of the ink of the present invention, can be maintained.

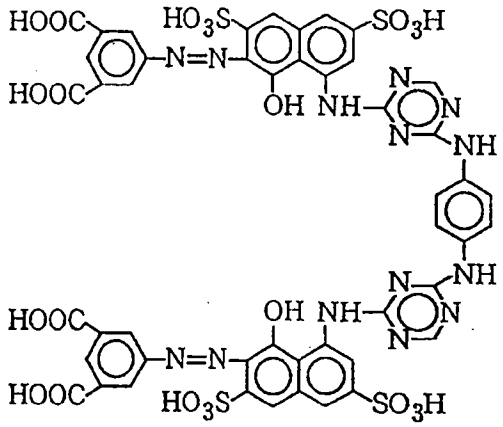
4. Colorants (dyes)

The colorant used in the present invention is a water-soluble dye. Any known dyes so long as it is a water-soluble dye for use in water-based ink-jet ink may be used in the present invention.

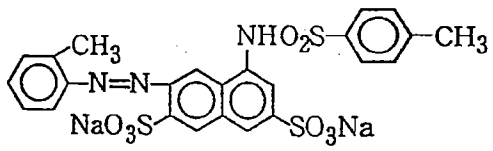
Examples of water-soluble dyes preferably used in the ink according to the present invention are shown below. These dyes are belonging to a group of substances which are clear in color tone and dissolved stably in an ink medium and have been selected for the sake of recording images exhibiting an excellent color tone when recorded on paper and a good water-fastness on a recorded material. Specifically, the following are exemplified, but the present invention is by no means limited to these. Also, the water-solubilizing groups in the exemplified dyes may be each in free acidic states,

alkali metal salts, ammonium salts, or organic amine salts.

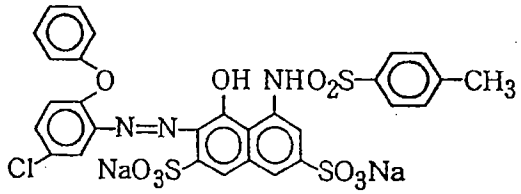
Magenta dye (1)



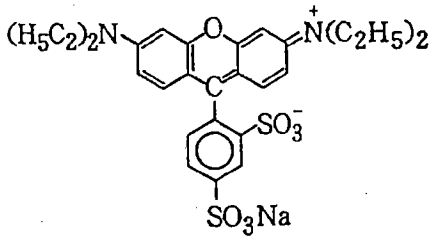
Magenta dye (2)



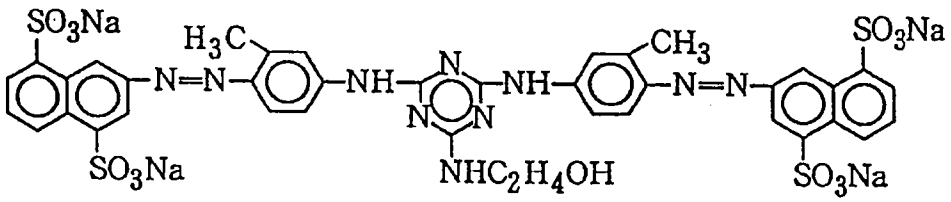
Magenta dye (3)



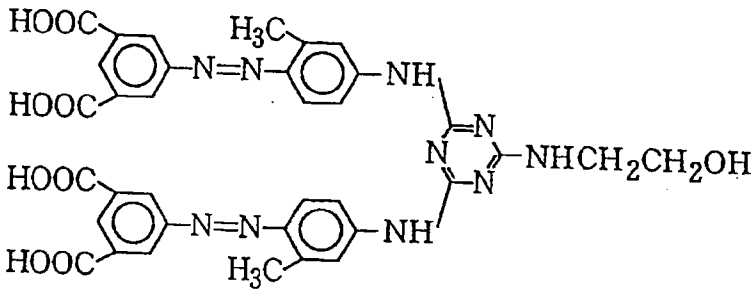
Magenta dye (4)



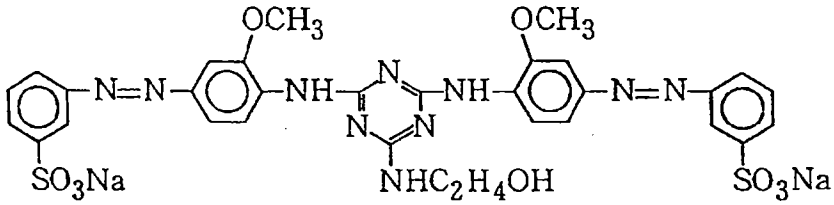
Yellow dye (1)



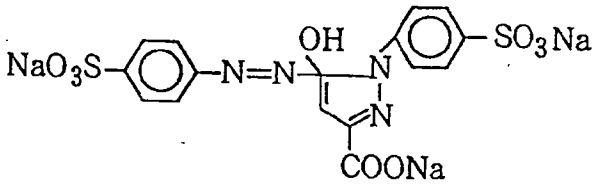
Yellow dye (2)



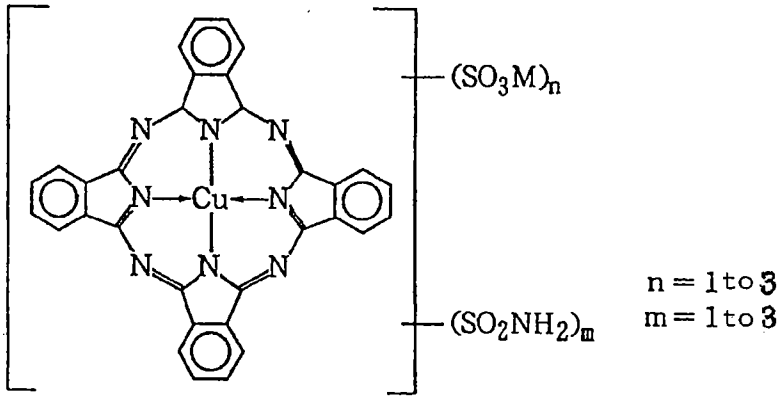
Yellow dye (3)



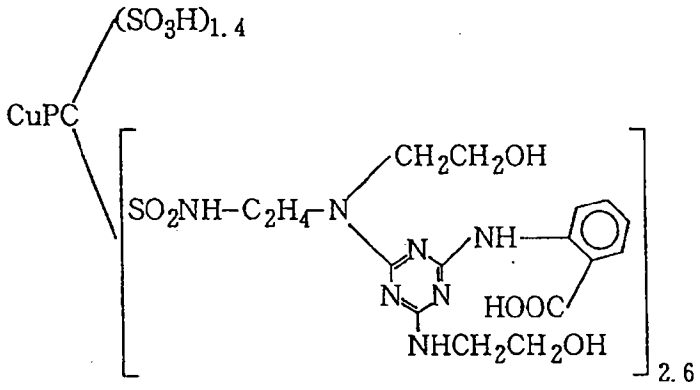
Yellow dye (4)



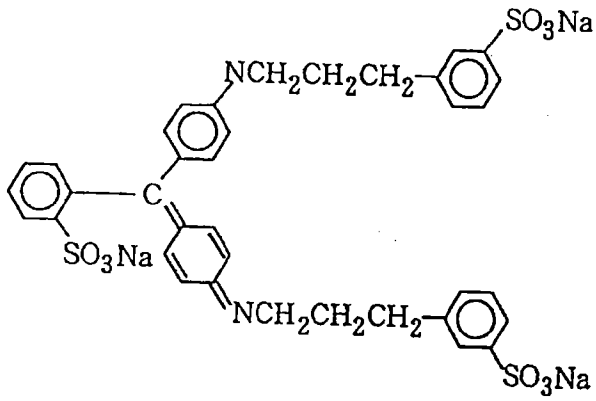
Cyan dye (1)



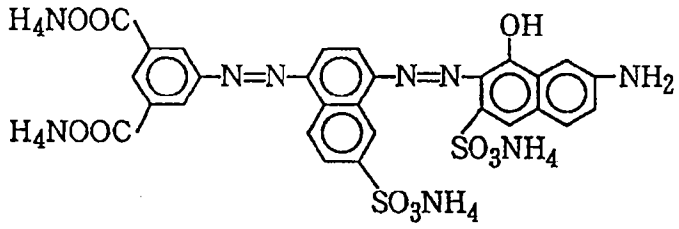
Cyan dye (2)



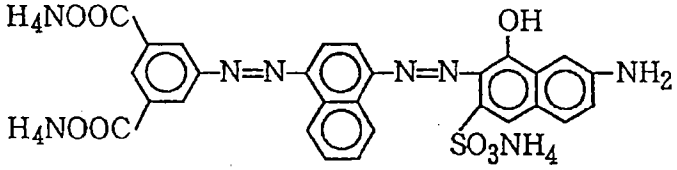
Cyan dye (3): ABL-9, Triphenyl methane type



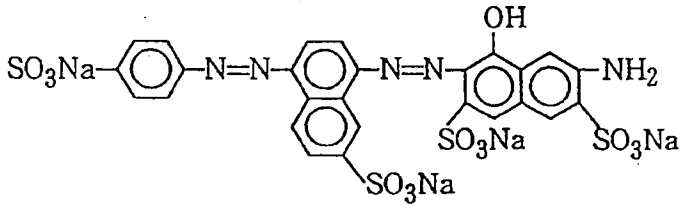
Black dye (1)



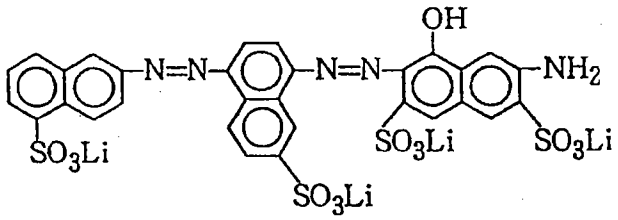
Black dye (2)



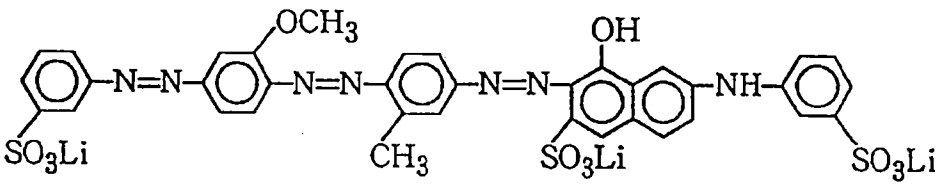
Black dye (3)



Black dye (4)



Black dye (5)



While the aforementioned dyes are compounds which are appropriate for an ink for an ink-jet recording method, it is needless to say that appropriate dyes may be selected from water-soluble dyes other than these such as acid dyes or direct dyes. The amount of such water-soluble dyes to be used is approximately 0.5 to 5.0% by weight based on the total weight of an ink.

5. Liquid medium for ink

The liquid medium of the ink is described below. Although water alone may be sued as the liquid medium for the ink of the present invention, it is preferable to add water-miscible organic solvents with a high moisture-maintaining property for obtaining a more reliable ink. Specifically, examples of such include the following: ethylene glycol, diethylene glycol, triethylene glycol, tripropylene glycol, glycerin, 1,2,4-butane triol, 1,2,6-hexane triol, 1,2,5-pentane triol, 1,2-butane diol, 1,3-butane diol, 1,4-butane diol, dimethyl sulfoxide, diacetone alcohol, glycerin monoallyl ether, propylene glycol, butylene glycol, polyethylene glycol 300, tiodiglycol, N-methyl-2-pyrrolidine, 2-pyrrolidine, γ-butyro lactone, 1,3-dimethyl-2-imidazolidinone, sulfolane, trimethylol propane, trimethylol ethane, neopentyl glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monoisoprpyl ether, ethylene glycol monoallyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, bis β-hydroxyethyl sulfone, bis β-hydroxyethyl urea, urea, acetonyl acetone, pentaerythritol, 1,4-cyclohexane diol, and the like. These water-soluble organic solvents are preferably used at a ratio of 5 to 50 parts by weight to 100 parts by weight of water.

6. pH adjusting agents

A pH value of the ink of the present invention should preferably be adjusted so as to be neutral to basic, owing to properties of the water-soluble dye to be used, from the view point of stability of the ink. Specific examples of pH adjusting agents to be used for this purpose include the following: organic bases such as ethanolamine, diethanolamine, triethanolamine, N-methyl ethanolamine, N-ethyl diethanolamine, 2-amino-2-methyl propanol, 2-ethyl-2-amino-1,3-propane diol, 2-(2-amino ether)ethanolamine, tris(hydroxy methyl) amino methane, ammonia, glycine, glycyl glycine, histidine, L-lysine, L-arginine, piperidene, morphorine, bis β-hydroxyethyl urea, and the like; and bases such as sodium hydroxide, potassium hydroxide, lithium hydroxide, and the like. It is possible to provide an ink with a pH stability by means of a pH buffer agent. Of these bases, alcohol amine is particularly preferable for obtaining storability of the ink and a good ejection stability of the ink when used in an ink-jet recording apparatus.

7. Adjustment of the ink

The ink according to the present invention is adjusted as follows.

The ink according to the present invention is adjusted so as to have a surface tension of not less than 30 mN/m, preferably from 35 to 45 mN/m, and a viscosity is not more than 5 mPa • s, preferably from 2 to 4 mPa • s. In order to obtain such physical properties, the mixture must include substance selected from Compound Group A in an amount of from 6% to 15% by weight, and substance selected from Compound Group B in an amount of from 0.5% to 5% by weight. Regarding a range of selecting ink-materials and a physical property range, the above physical property range must take precedence.

While the ink according to the present invention can be used favorably with ink-jet recording apparatus, it is needless to say that the ink according to the present invention is not limited to such, but may be applied to other monocolor ink-jet recording systems and other recording systems.

8. Method of conducting color ink-jet recording

Next, the method of conducting color ink-jet recording according to the present invention will be described.

The ink according to the present invention is optimally designed for on-demand type high-quality ink-jet printers. The basic configuration of such a printer is an apparatus with a multi-nozzle recording head having piezoelectric devices or thermal emitting devices, in which recording is conducted at a nozzle density of not less than 180 dpi (dots per inch), a droplet volume of from 3 to 50 pl, more preferably from 10 to 20 pl (pico-liter) and at a recording density of not less than 300 lpi (lines per inch). Also, the ink according to the present invention is suitable for recording apparatus of such a type where the ink tank alone is replaced when the ink has been spent.

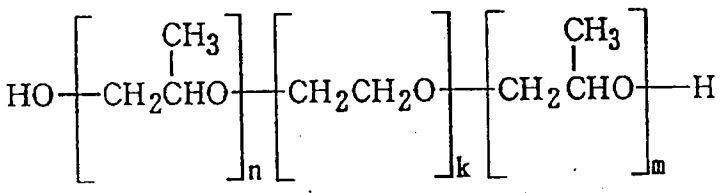
Next, the present invention will be described in further detail with reference to Examples and Comparative Examples. In the following Examples and Comparative Examples, the terms "parts" and "%" respectively refer to "parts by weight" and "% by weight", unless otherwise specified.

Example 1

- Ammonium salt of Black dye (1) 3 parts
- Compound A-9 10 parts

  (Adduct product of 2 mol of ethylene oxide to 1 mol of benzyl alcohol)
- Compound C-1 4 parts

  (50% isopropyl alcohol solution of a liquid compound of the formula



  wherein n + m = 16, k = 12, molecular weight is ca. 1,450, HLB = 7.3 (calculated value))
- Ethylene glycol 10 parts
- Tris(hydroxymethyl)amino methane 1 part

  (pH adjuster)
- Water 72 parts

The above ingredients were well stirred and mixed, and filtered through a membrane filter having a pore size of 0.2 µm under pressure, thereby obtaining Black ink GEI-1B according to the present Example, having pH of 8.3, surface tension of 42.0 mN/m, and viscosity of 2.2 mPa•s. Further, cyan (GEI-1C), magenta (GEI-1M), and yellow (GEI-1Y)

inks were prepared in the same way, except that the dye thereof was replaced with those described in Table 1.

Table 1

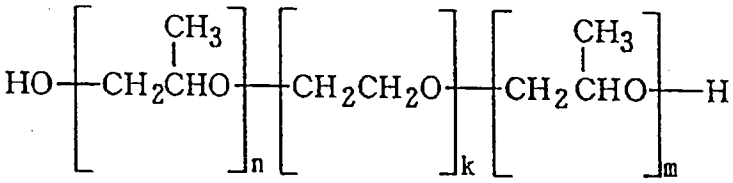
Name of ink	Dye	Viscosity (mPa • s)	Surface tension (mN/m)
GEI-1C	Cyan dye (2)	2.2	41.0
GEI-1M	Magenta dye (1)	2.3	43.0
GEI-1Y	Yellow dye (2)	2.15	40.0

Example 2

- Ammonium salt of Cyan dye (2) 2.8 parts
- Compound A-8 8 parts

  (dipropylene glycol monopropyl ether)
- Compound C-1 4 parts

  (50% ethyl alcohol solution of a liquid compound of the formula



wherein n + m = 30, k = 25, molecular weight is ca. 2,850, HLB = 7.7 (calculated value))
- Diethylene glycol 13 parts
- Ammonium sulfate (pH adjuster) 1 part
- Water 71.2 parts

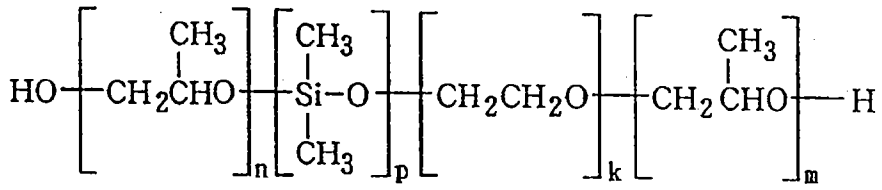
The above ingredients were well stirred and mixed, and filtered through a membrane filter having a pore size of 0.2 µm under pressure, thereby obtaining Cyan ink GEI-2C according to the present Example, having pH of 8.5, surface tension of 36.0 mN/m, and viscosity of 2.5 mPa • s. Further, magenta (GEI-2M), yellow (GEI-2Y), and black (GEI-2B) inks were prepared in the same way, except that the dye thereof was replaced with those described in Table 2.

Table 2

Name of ink	Dye	Viscosity (mPa • s)	Surface tension (mN/m)
GEI-2M	Magenta dye (1)	2.3	37.5
GEI-2Y	Yellow dye (2)	2.3	37.4
GEI-2B	Black dye (2)	2.1	38.0

Example 3

- Ammonium salt of Magenta dye (1) 2.8 parts
- Compound A-7 6 parts
  (triethylene glycol n-butyl ether)
- Compound C-2 4 parts
  (50% methanol solution of a compound of the formula



wherein n + m = 20, p = 5, k = 20, and molecular weight is ca. 2,500)

- Diethylene glycol 15 parts
- Triethanol amine (pH adjuster) 1 part
- Water 72.2 parts

The above ingredients were well stirred and mixed, and filtered through a membrane filter having a pore size of 0.2 µm under pressure, thereby obtaining Magenta ink GEI-3M according to the present Example, having pH of 9.0, surface tension of 40.0 mN/m, and viscosity of 2.1 mPa • s. Further, black (GEI-3B), cyan (GEI-3C), and yellow (GEI-3Y) inks were prepared in the same way, except that the dye thereof was replaced with those described in Table 3.

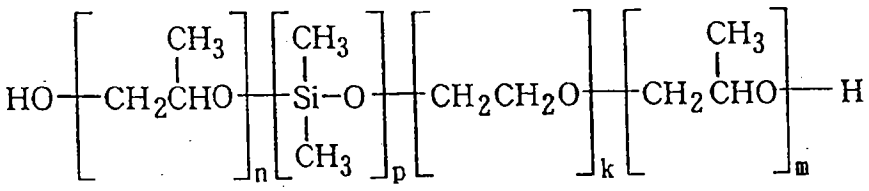
Table 3

Name of ink	Dye	Viscosity (mPa • s)	Surface tension (mN/m)
GEI-3B	Black dye (2)	2.2	39.3
GEI-3C	Cyan dye (1)	2.4	39.5
GEI-3Y	Yellow dye (4)	2.2	40.2

Example 4

- Ammonium salt of Yellow dye (2) 2.8 parts
- Compound A-2 (SURFINOL 465) 1.5 parts
- Compound C-2 5 parts

(20% methanol solution of a compound of the formula



wherein n + m = 50, p = 3, k = 30, and molecular weight is ca. 4,500)

- Glycerin 8 parts
- Diethylene glycol 15 parts
- Triethanol amine (pH adjuster) 1 part
- Water 72.2 parts

The above ingredients were well stirred and mixed, and filtered through a membrane filter having a pore size of 0.2 µm under pressure, thereby obtaining Yellow ink GEI-4Y according to the present Example, having pH of 9.2, surface tension of 35.0 mN/m, and viscosity of 2.7 mPa • s. Further, black (GEI-4B), magenta (GEI-4M), and cyan (GEI-4C) inks were prepared in the same way, except that the dye thereof was replaced with those described in Table 4.

Table 4

Name of ink	Dye	Viscosity (mPa • s)	Surface tension (mN/m)
GEI-4B	Black dye (4)	2.6	35.2
GEI-4M	Magenta dye (4)	2.7	36.5
GEI-4C	Cyan dye (2)	2.6	36.0

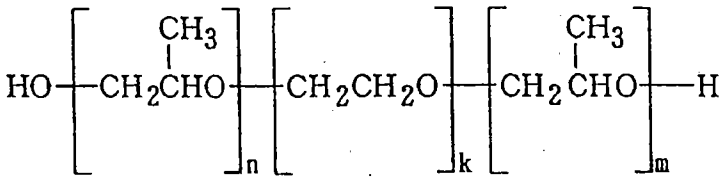
Example 5

- Ammonium salt of Black dye (2) 2.8 parts
- Compound A-8 10 parts
  (dipropylene glycol monopropyl ether)
- Compound B-2 2 parts
  (Surface active agent of ethylene oxide -

propylene oxide - ethylene oxide-type, with HLB = 8 and molecular weight of 2,500)

- Compound C-1 4 parts

(50% ethyl alcohol solution of a compound of the formula



wherein n + m = 30, k = 25, molecular weight ca. 2,850, HLB = 7.7 (calculated value))

- Diethylene glycol 5 parts
- Glycerin 10 parts
- Lithium hydroxide (pH adjuster) 0.3 parts
- Water 72.2 parts

The above ingredients were well stirred and mixed, and filtered through a membrane filter having a pore size of 0.2 µm under pressure, thereby obtaining Black ink GEI-5B according to the present Example, having pH of 9.5, surface tension of 38.0 mN/m, and viscosity of 3.0 mPa • s. Further, cyan (GEI-5C), magenta (GEI-5M), and yellow (GEI-5Y) inks were prepared in the same way, except that the dye thereof was replaced with those described in Table 5.

Table 5

Name of ink	Dye	Viscosity (mPa • s)	Surface tension (mN/m)
GEI-5C	Cyan dye (2)	2.9	37.5
GEI-5M	Magenta dye (2)	2.8	38.0
GEI-5Y	Yellow dye (2)	2.9	39.0

Comparative Example 1

Ink SFI-1B of Comparative Example 1 the penetration of which is increased by means of a surface active agent was prepared with the following ingredients:

• Ammonium salt of Black dye (1)	3 parts
• Ethylene oxide adduct of nonyl phenol (HLB = 10, manufactured by SANNOPCO CO., LTD)	1 part
• Urea	7.5 parts
• Diethylene glycol	12.5 parts
• Tris(hydroxymethyl) amino methane (pH adjuster)	1 part
• Water	75 parts

The above ingredients were well stirred and mixed, and filtered through a membrane filter having a pore size of 0.2 µm under pressure, thereby obtaining Black ink SFI-1B of Comparative Example 1, having pH of 8.0, surface tension of 30.0 mN/m, and viscosity of 2.5 mPa • s.

Comparative Example 2

Ink SFDFI-2B of Comparative Example 2 in which silicone foaming-resistant agent is added for retarding foaming was prepared with the following ingredients:

• Ammonium salt of Black dye (1)	3 parts
• Ethylene oxide adduct of nonyl phenol (HLB = 10, manufactured by SANNOPCO CO., LTD)	1 part
• Urea	7.5 parts
• Diethylene glycol	12.5 parts
• Tris(hydroxy methyl) amino methane (pH adjuster)	1 part
• Co-polymer of silicone diol and ethylene oxide (foam-removing agent)	2 parts
• Water	73 parts

The above ingredients were well stirred in a homogenizer at 100 rpm for 15 minutes, and filtered through a membrane filter having a pore size of 0.2 µm under pressure, thereby obtaining Black ink SFDFI-2B of Comparative Example 2, having pH of 8.0, surface tension of 26.5 mN/m, and viscosity of 2.6 mPa • s. This ink was in a state where the foaming-resistant agent was more emulsified, and the solution was somewhat lacking in transparency.

Comparative Example 3

Black ink CSFI-3B of Comparative Example 3 was obtained in the same way as with Example 1, except for reducing the amount of Compound A-9 (Ethylene oxide 2 mol adduct of benzyl alcohol) from 10 parts to 4 parts, and adding diethylene glycol instead. The viscosity of this ink was 2.55 mPa • s, and the surface tension was 44.0 mN/m.

Printing test:

The following tests were conducted for the inks of Examples 1 to 5 and Comparative Examples 1 to 3, using a test bubble jet color printer having 128 nozzles, nozzle density of 720 dpi, main scanning and sub-scanning print density 720 lpi, driving speed of 8 kHz, and average droplet volume of 10 pl, and using paper for electrophotography (plain-paper).

1. Ejection properties - droplet formation

An apparatus which can monitor the form (volume) of droplets being ejected from the nozzle was used to measure the average value of the droplet volume.

(Evaluation standards)

A: Main droplets of approximately 10 pl were ejected.
B: 2 droplets having a volume smaller than 10 pl were ejected.
C: The ink was not forming droplets, being ejected in the form of liquid columns.
D: Many small droplets were being ejected disruptedly.

2. Ink tank replacement test

All the ink in an ink tank was used, a new ink tank of the same ink color was mounted, suction was conducted from the nozzle side using a recovery pump, and the head was filled with the new ink. Subsequently, continuous solid printing was conducted until the ink was spent.

(Evaluation standards)

A: Printing was conducted for the normal number of pages, without problem.
B: Ink stopped once during the operation, but returned to normal conditions with a recovery operation.
C: Ink stopped often, and pump suction operations were conducted frequently. There were observed many small bubbles in the ink chamber after the test, but there was no damage on the heater.
D: Ink stopped entirely, the print density became light, and printing could not be continued even after recovery operations were conducted. There were observed many small bubbles in the ink chamber after the test, and that there was damage also observed on the heater.

3. Print suitability - drying property

Test patterns with a text and monocolor patches arrayed were recorded to the aforementioned plain paper, and the time required for drying was measured.

(Evaluation standards)

A: The print was dry when paper is discharged from the printer.
B: The print dried in several seconds after paper is discharged.
C: The print dried in several ten seconds after paper is discharged.

4. Print quality - Border bleeding

The borders between the color patches and the characters of the printed material obtained in "3. Print suitability - driability" was examined for bleeding.

(Evaluation standards)

A: No border bleeding could be discerned by eye.
B: Some border bleeding occurred between the yellow and black.
C: The characters with somewhat thicker, and border bleeding was marked.

In the case of the test for the inks of Comparative Examples, the color inks of Example 1 were used, except for the black ink.

Test results:

The evaluation results of each of the items of the aforementioned printing tests were shown in Table 6.

Table 6

Evaluation results of Examples 1 to 5 and Comparative Examples 1 to 3.				
	1. Ejection properties - droplet formation	2. Ink tank replacement test	3. Print suitability - drying property	4. Print quality - Border bleeding
Example 1	A	A	A	A
Example 2	A	A	A	A
Example 3	A	A	A	A
Example 4	A	A	A	A
Example 5	A	A	A	A
Comparative Example 1	B	C	A	B
Comparative Example 2	C	A	B	C
Comparative Example 3	A	C	B	C

Thus, as described above, according to the present invention, there can be provided a novel ink which does not easily allow for trouble within a color ink-jet recording apparatus such a foaming-up of ink or an air inclusion in the ink, and therefore, there can be provided an ink which can be supplied stably to the nozzles, which ink further has a good balance between penetration into the recording paper and bleeding, which has stable ejection properties so as to allow for stable formation of droplets even when dealing with small droplet formation, and moreover which does not easily cause clogging, thus allowing for high-quality recording, and at the same time, providing a color ink-jet recording system which also has excellent reliability.

Also, inexpensive and high-quality images can be realized in the office by means of employing the ink of the present invention, and thus is meaningful to widespread general use of digital printing technology.

Moreover, by means of using the ink of the present invention in ink-jet recording apparatuses effects can be obtained such as: stable droplet formation can be maintained without separating into smaller droplets, a phenomena called splashing, and ejecting can be conducted for long periods of time; the penetration-fixing time is short, coloring is good, bleeding is minimal, thus providing a clear image, even when plain paper is used; and further, when used in an ink-jet recording apparatus which allows for the ink tank alone to be replaced, there is little air taken in or foaming in the ink even when replacing the ink tank, so that the ink path is properly filled with ink.

Claims

1. An ink, having a surface tension of not less than 30 mN/m and a viscosity of not more than 5 mPa • s, and comprising a water-soluble dye, water, at least one compound selected from the Compound Groups A and B, and at least one compound selected from the Compound Group C:

Compound Group A:

A-1: Ethylene glycol mono-n-butyl ether,
A-2: Ethylene glycol monophenyl ether,
A-3: Ethylene glycol monoisobutyl ether,
A-4: Diethylene glycol mono-n-butyl ether,
A-5: Diethylene glycol monohexyl ether,
A-6: Diethylene glycol monoisobutyl ether,
A-7: Triethylene glycol n-butyl ether,
A-8: Dipropylene glycol monopropyl ether, and
A-9: Ethylene oxide adduct of benzyl alcohol;

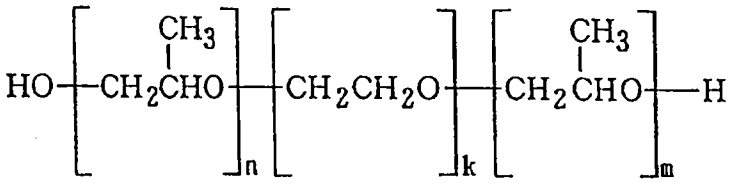
Compound Group B:

B-1: Surface active agent of ethylene oxide adduct of acetylene glycol-type,
B-2: Surface active agent of ethylene oxide - propylene oxide - ethylene oxide-type surface, and

B-3: Ethylene oxide adduct of higher alcohol; and

Compound Group C:

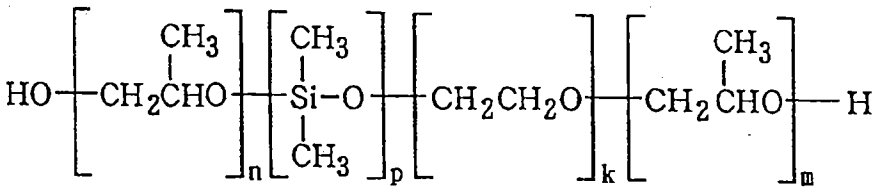
C-1: A compound of the formula



C − 1

wherein k is an integer of 3 to 50, m is an integer of 3 to 25, n is an integer of 3 to 25, and n + m is an integer of 6 to 50, and

C-2: A compound of the formula



C − 2

wherein k is an integer of 20 to 50, m is an integer of 10 to 25, n is an integer of 10 to 25, n + m is an integer of 20 to 50, and p is an integer of 2 to 5.

2. The ink according to Claim 1, wherein a compound of Compound Group A is present in an amount of from 6 to 12% by weight based on the total weight of said ink.

3. The ink according to Claim 1, wherein a compound of Compound Group B is present in an amount of from 0.3 to 3.0% by weight based on the total weight of said ink.

4. The ink according to Claim 1, wherein a compound of Compound Group C is present in an amount of from 0.5 to 5.0% by weight based on the total weight of said ink.

5. The ink according to Claim 1, wherein said water-soluble dye is present in an amount of from 0.5 to 5.0% by weight based on the total weight of said ink.

6. The ink according to Claim 1, which further comprises water-soluble organic solvent.

7. The ink according to Claim 1, wherein said water-soluble dye is a magenta dye.

8. The ink according to Claim 1, wherein said water-soluble dye is a yellow dye.

9. The ink according to Claim 1, wherein said water-soluble dye is a cyan dye.

10. The ink according to Claim 1, wherein said water-soluble dye is a black dye.

11. A color ink-jet recording method for conducting a color recording by applying respective ink droplets which are made from using magenta, yellow, cyan, and black inks by means of an ink-jet system, wherein said inks are each an ink according to Claim 1.

12. A color ink-jet recording method for conducting a color recording by applying respective ink droplets which are

made from using magenta, yellow, cyan, and black inks by means of an ink-jet system, a volume per droplet is adjusted so as to be from 3 to 50 picoliters, wherein said inks are each an ink according to Claim 1.

13. Use of an ink according to any of the Claims 1 through 10 in ink-jet recording.

14. Use of an ink according to any of the Claims 1 through 10 in color recording.

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(54) Ink, and a color ink-jet recording method using the same

(57) Provided is an ink, having a surface tension of not less than 30 mN/m and a viscosity of not more than 5 mPa • s, and comprising a water-soluble dye, water, at least one compound selected from the Compound Groups A and B, and at least one compound selected from the Compound Group C.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 6804

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 250 271 A (CANON) * example 1 * ---	1-14	C09D11/00
X	EP 0 592 774 A (CANON) * page 4, line 3 - page 6, line 1 * ---	1-14	
X	US 5 382 283 A (FUJI XEROX) * examples 8-10 * -----	1-14	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 July 1997	Schmidt, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document

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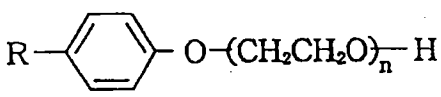
(54) Ink, ink-jet recording method, and ink-jet recording apparatus.

(57) Provided is an ink for ink-jet recording, comprising a dye, water, and the components (a), (b), and (c) below: (a) at least one surfactant selected from the group consisting of higher alcohol-ethylene oxide adducts represented by General Formula [1], alkylphenol-ethylene oxide adducts represented by General Formula [2], ethylene oxide-propylene oxide copolymers represented by General Formula [3], and acetylene glycol-ethylene oxide adducts represented by General Formula [4], at a content of from 0.1 to 20 % by weight;

$$R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}H \qquad [1]$$

where R is alkyl, and n is an integer;



[2]

where R is alkyl, and n is an integer;

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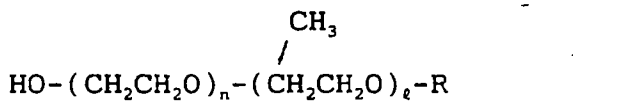
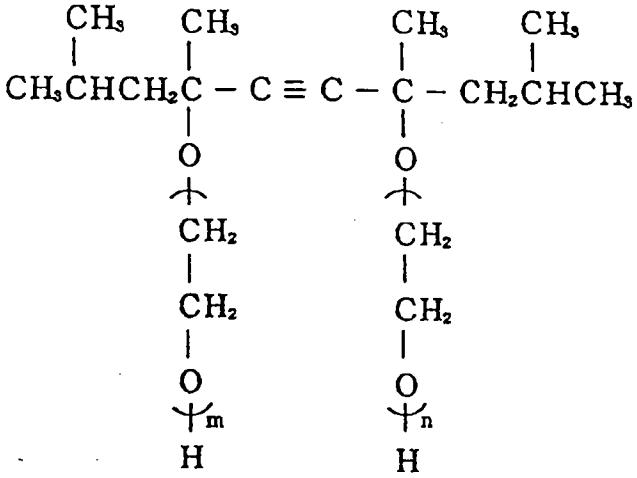


[3]

where R is alkyl, and n and ℓ are respectively an integer;



[4]

where m and n are respectively an integer;
(b) thiodiglycol; and
(c) urea or an derivative thereof.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to an ink which provides excellent color recording on plain paper such as wood-free paper, medium-quality paper, bond paper, and paper for copying. The present invention also relates to an ink-jet recording method, and an ink-jet recording apparatus employing the above ink.

Related Background Art

Personal computers including desk-top types, lap-top types, and book types have come to employ a color display unit in recent years. Software is also directing to color representation. Consequently, printers are changing from monocolor types to color types.

Among recording methods employed by such printers, ink-jet recording is attracting attention. In the ink-jet recording, ink droplets are ejected and are attached to a recording medium such as paper sheets, converted paper sheets, plastic films, and cloths without contact of a recording head with the recording medium. The ink-jet recording method is advantageous in that noise is not produced because of non-contact of the recording head with the recording medium, and high speed printing and color recording is practicable.

In the ink-jet recording method, it is required that (1) ink does not cause running of ink at the recorded portion on the recording medium, (2) ink is sufficiently stable during storage, and (3) the safety is high. In color ink-jet recording, it is further required that (4) mixing (or bleeding) of different colors of inks caused by unfixed ink droplets does not occur on contact of different color inks on a recording medium, (5) a solid color portion is uniform in color, and (6) failure of ink ejection does not occur after interruption of ink ejection (first-ejection difficulty), since limited colors of inks are more frequently used in color printing unlike monocolor printing.

However, conventional inks per se are not usable as inks for color recording because they cause serious bleeding and do not give high-quality images. Presumably, the bleeding is caused by the fact that the ink is dotted before the previously dotted different color of ink has been sufficiently fixed. Coat paper, which has high ink-absorbing ability, is used for color recording in order to prevent the bleeding. Further, for printing on plain paper such as paper for copying and bond paper, a printing method reflecting upon the fixing time of ink is proposed in which ink is dotted after the previously dotted ink droplet has been fixed. In such a printing method, speed of paper feed have to be slowed down disadvantageously, thereby the printing time becomes longer irrespectively of the ink-dotting method. Therefore, high speed printing which is characteristic of ink-jet recording cannot be practised with such a printing method.

To shorten the fixing time, Japanese Patent Application Laid-Open No. 55-29546 discloses a method in which a surfactant is incorporated into ink in a larger amount than usual and thereby the ink seems to become dry instantaneously owing to the increased penetration power of ink afforded by the surfactant. However, the simple addition of a surfactant in a larger amount as above cannot prevent mixing of different colors of inks at the border of colors even though it improves the ink fixation. Moreover, it augments penetration of ink toward the back face of the paper, which lowers color density on the paper face, or causes nonuniform dyeing of a fiber layer on the paper surface, resulting in irregularity of color density in solid printing area and deterioration of image quality.

Furthermore, feathering and ink fixation on a plain paper are improved by use of strongly alkaline ink (see Japanese Patent Application Laid-Open No. 56-57862, etc.), or by use of a specific kind of ink (see Japanese Patent Application Laid-Open No. 56-5871, etc.). These inks, however, do not always prevent bleeding satisfactorily, and even in the case where the bleeding is relatively slight, the feathering is conspicuous (not satisfying the aforementioned requirement (1) of the prior art) or ejection failure is liable to occur (not satisfying the aforementioned requirement (6) of the prior art). As above, no color ink has been obtained which satisfies all the above requirements and gives high quality of an image with high speed on plain paper.

SUMMARY OF THE INVENTION

The present invention intends to provide an ink for ink-jet recording which is capable of forming a color image of high quality at high and uniform color density on a usual recording medium such as plain paper without feathering or ink-bleeding, and especially without mixing of different colors of inks at the color border.

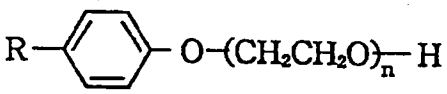
The present invention also intends to provide an ink-jet recording method, and an ink-jet recording apparatus employing the above ink.

According to a first aspect of the present invention, there is provided an ink for ink-jet recording which contains a dye and water, and further comprises the components (a), (b), and (c) below:

(a) at least one surfactant selected from the group consisting of higher alcohol-ethylene oxide adducts represented by General Formula [1], alkylphenolethylene oxide adducts represented by General Formula [2], ethylene oxide-propylene oxide copolymers represented by General Formula [3], and acetylene glycol-ethylene oxide adducts represented by General Formula [4], at a content of from 0.1 to 20 % by weight based on the total weight of the ink;

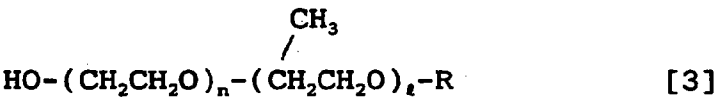
$$R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}H \qquad [1]$$

where R is alkyl, and n is an integer;



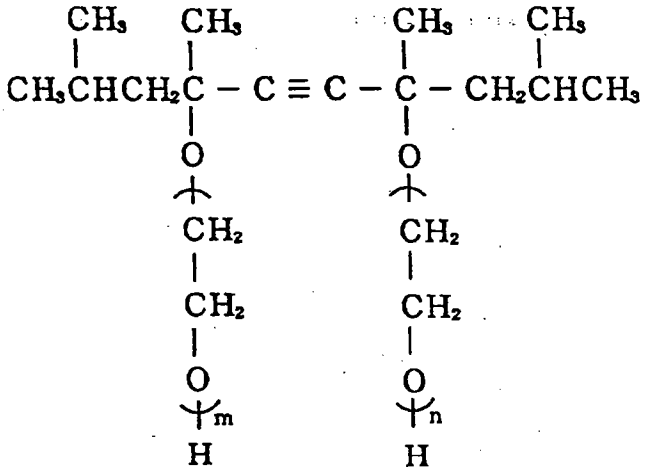
[2]

where R is alkyl, and n is an integer;



[3]

where R is alkyl, and n and ℓ are respectively an integer;



[4]

where m and n are respectively an integer;

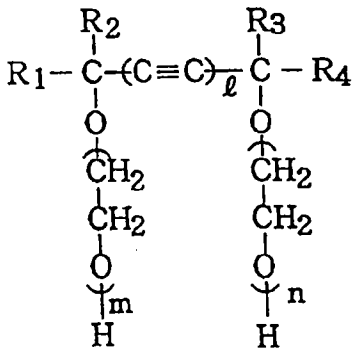
(b) thiodiglycol; and

(c) urea or an derivative thereof.

According to a second aspect of the present invention, there is provided an ink-jet recording method which conducts recording on a recording medium with droplets of ink, which comprises dye, water, and the aforementioned components (a), (b), and (c).

According to a third aspect another aspect of the present invention, there is provided a color ink-jet recording method which conducts recording by ejecting droplets of inks of two or more colors to adjacent or superposed positions on a recording medium, using the ink comprising a dye, water and the aforementioned components (a), (b), and (c).

According to a fourth aspect of the present invention, there is provided an ink which comprises a dye, a water-soluble organic solvent, water, and a compound of the formula;



[5]

where R_1, R_2, R_3, and R_4 are respectively hydrogen, an alkyl or alkenyl group of 1 to 4 carbon atoms, or a substituted or unsubstituted phenyl group; and m+n is ranging from 0 to 50; and ℓ is a number of 2 or more.

According to a fifth aspect of the present invention, there is provided an ink-jet recording method which conducts recording with droplets of ink on a recording medium, using the ink comprising a dye, water-soluble organic solvent, water, and a compound represented by General Formula [5] above.

According to a sixth aspect of the present invention, there is provided a color ink-jet recording method which conducts recording by ejecting droplets of ink of two or more colors to adjacent or superposed positions on a recording medium, using the ink comprising a dye, water and the aforementioned compound represented by General Formula [5] above.

According to a seventh aspect of the present invention, there is provided a recording unit comprising an ink container portion for holding ink and a head for ejecting the ink as ink droplets, in which the ink is the one specified in the above first or fourth aspect of the present invention.

According to a eighth aspect of the present invention, there is provided an ink cartridge comprising an ink container portion for holding ink, in which the ink is the one specified in the above first or fourth aspect of the present invention.

According to ninth aspect of the present invention, there is provided an ink-jet recording apparatus comprising the recording unit of the seventh aspect of the present invention, wherein the ink of the above first or fourth aspect of the present invention is employed.

According to a tenth aspect of the present invention, there is provided a ink-jet recording apparatus, comprising an ink cartridge of the eighth aspect of the present invention, and a recording head.

According to an eleventh aspect of the present invention, there is provided a color ink-jet recording method in which droplets of two or more color inks are ejected in accordance of pulse signal to adjacent or superposed positions on a recording medium, and in which the ink comprises a nonionic surfactant in an amount of from 1.0 to 20.0 % by weight, the ink ejected for one pulse is in an amount of from 10 to 70 pℓ, and the feathering rate (A) defined by Equation [I] is in the range of from 2.5 to 3.5:

$$A = B/C \quad [I]$$

where B is a diameter (μm) of a dot formed on plain paper, and C is a diameter (μm) of the ejected ink droplet.

According to a twelfth aspect of the present invention, there is provided color ink-jet recording apparatus which conducts recording by ejecting droplets of two or more color inks onto adjacent or superposed positions on a recording medium, said apparatus comprises a recording means for conducting recording mode, by use of an ink containing a nonionic surfactant in an amount of from 1.0 to 20.0 % by weight, by ejecting the ink for one pulse in an amount of from 10 to 70 pℓ to form ink dots at the feathering rate (A) defined by Equation [I] is in the range of from 2.5 to 3.5:

$$A = B/C \quad [I]$$

where B is a diameter (μm) of a dot formed on plain paper, and C is a diameter (μm) of the ejected ink

droplet.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows an example of the pattern of dotting of different color inks.

Fig. 2 shows another example of the pattern of dotting of different color inks.

Fig. 3 is a longitudinal cross-sectional view of a head portion of an ink-jet recording apparatus of the present invention.

Fig. 4 is a transverse cross-sectional view of a head portion of an ink-jet recording apparatus of the present invention.

Fig. 5 is a perspective view of a head portion of an ink-jet recording apparatus of the present invention.

Fig. 6 is a perspective view of an ink-jet recording apparatus of the present invention.

Fig. 7 is a longitudinal sectional view of an ink cartridge of the present invention.

Fig. 8 is a perspective view of a recording unit of the present invention.

Fig. 9 is a perspective view of a recording portion in which a plurality of recording heads are arranged and which was used in an example of the present invention.

Fig. 10 is a perspective view of another recording head used in the present invention.

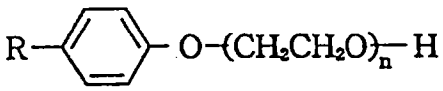
DESCRIPTION OF THE PREFERRED EMBODIMENT

The inventors of the present invention have studied comprehensively a method of color image formation which does not causes bleeding of ink and gives a uniform color image without irregularity of colors. As the result, it has been found as a first invention that an ink containing the components (a), (b), and (c) below is extremely effective:

(a) at least one surfactant selected from the group consisting of higher alcohol-ethylene oxide adducts represented by General Formula [1], alkylphenol-ethylene oxide adducts represented by General Formula [2], ethylene oxide-propylene oxide copolymers represented by General Formula [3], and acetylene glycol-ethylene oxide adducts represented by General Formula [4], at a content of from 0.1 to 20 % by weight;

$$R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}H \qquad [1]$$

where R is alkyl, and n is an integer;

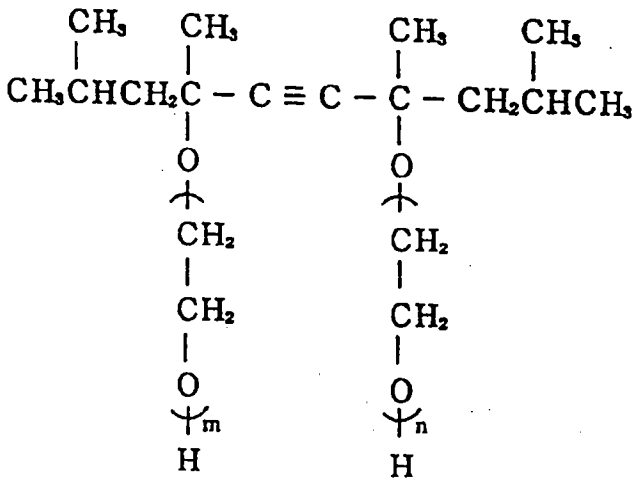


[2]

where R is alkyl, and n is an integer;

$$HO\text{-}(CH_2CH_2O)_n\text{-}(CH(CH_3)CH_2O)_\ell\text{-}R \qquad [3]$$

where R is alkyl, and n and ℓ are respectively an integer;



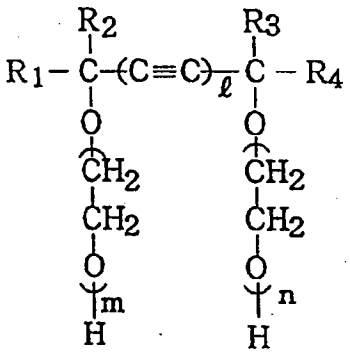
[4]

where m and n are respectively an integer;

(b) thiodiglycol; and

(c) urea or an derivative thereof.

As the further result of the study, it has been found as a second invention that an ink comprising the compound represented by General Formula (5) below is extremely effective:



[5]

where R_1, R_2, R_3, and R_4 are respectively hydrogen, an alkyl or alkenyl group of 1 to 4 carbon atoms, or a substituted or unsubstituted phenyl group; and m+n is ranging from 0 to 50; and ℓ is a number of 2 or more.

The inks of the first invention and the second invention are effective for formation of uniform images without bleeding or color irregularity presumably from the reasons below.

The most important factor which affects prevention of ink bleeding and uniformity of color of recorded images is considered to be the wettability of a recording medium by the ink, or a wetting power of the ink on the recording medium. Among the recording media, plain paper especially has fibers exposed on the recording surface, and the fiber density on the surface is not uniform. At the portion where the fiber density is high, the ink fixation is slow, whereby ink bleeds or color of an image becomes irregular. The ink which has a sufficient wetting power is considered to be fixed uniformly irrespectively of the paper fiber density, and to be free from bleeding and color irregularity. Further, the ink which has excellent wetting power is considered to form precisely circular dots with uniformity of color, thereby providing images of higher quality.

The first invention of the present invention will be described in detail.

The wetting power of the ink relates closely to the interaction between the ink and the recording material at the interface. Addition of a surfactant generally decreases the interfacial tension between the ink and the recording medium, and improves the wetting power of the ink. In particular, the nonionic surfactant having ethylene oxide chain as the component (a) of the first invention, when incorporated in the ink, the hydrophilic ethylene oxide portion of the surfactant presumably orients toward the recording medium to give

a specific uniform wettability. On the contrary, an ionic surfactant, which has a hydrophilic portion which has less affinity with the recording medium than the nonionic surfactant, does not exhibit such effect.

The ethylene oxide addition type nonionic surfactant in the present first invention is preferably added in an amount of from 0.1 to 20 %, more preferably from 0.1 to 5 % by weight based on the weight of the ink. The wetting power is not sufficient at the amount of the surfactant of less than 0.1 % by weight, while, addition of the surfactant in an amount exceeding 20 % by weight does not improve more the wetting property and is disadvantageous in production cost and ink reliability.

The addition number of the ethylene oxide unit, the hydrophilic portion, in the ethylene oxide addition type nonionic surfactant in the present first invention is preferably in the range of from 4 to 20, more preferably from 4 to 10 in terms of "n" or "n+m" in consideration of the affinity of the ethylene oxide moiety with the recording medium and orientation thereon. At the value of "n" or "n+m" of less than 4, the solubility of the surfactant is not sufficient to achieve the effect of the present invention, while at the value of more than 20, the excessive ethylene oxide is not necessarily effective and leads to slightly unstable ink ejection.

The medium for the aforementioned ethylene oxide addition type nonionic surfactant is described below.

Generally, the ethylene oxide addition type nonionic surfactant is inconvenient for stabilization of ink ejection because of its relatively high viscosity in consideration of ejection stabilization. Therefore, an additional water-soluble organic solvent is studied to improve the ink ejection without impairing the effects of the present invention. Consequently, thiodiglycol has been found to be satisfactory. The failure of ink ejection is caused generally by rise of viscosity resulting from vaporization of water at the nozzle. The use of thiodiglycol is considered to reduce more the rise of the viscosity than other solvents, thereby improving the ejection property. However, single use of thiodiglycol is not sufficiently effective yet for ejection stabilization. After comprehensive study, it has been found that combined use of thiodiglycol and urea or a derivative of urea improves greatly the ink ejection property. Presumably, the interaction between the thiodiglycol and urea or a urea derivative suppresses the rise of the viscosity specifically, and the dissolution of a dye is improved. The thiodiglycol and a urea derivative-thiourea derivative are used respectively in an amount of from 1 to 30 % by weight.

The amount of water used in the present first invention is preferably in the range of from 50 to 85 %, more preferably from 55 to 75 % by weight. If the amount of water is less than 50 %, the viscosity of the ink is relatively high, and the ejection stability tends to be relatively lower, even when thiodiglycol or urea or derivative thereof is used concurrently. If the amount of water is more than 85 %, the ethylene oxide portion, which is the hydrophilic portion of the ethylene oxide addition type nonionic surfactant, is relatively free, resulting in less orientation thereof and less uniformity.

The water-soluble organic solvents constituting the ink of the present first invention include polyalkylene glycols such as polyethylene glycol, and polypropylene glycol; alkylene glycols having 2 to 6 carbon atoms such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, hexylene glycol, and diethylene glycol; glycerin; 1,2,6-hexanetriol; lower alkyl ether of polyhydric alcohols such as ethylene glycol methyl ether, diethylene glycol methyl (or ethyl) ether, and triethylene glycol monomethyl (or ethyl) ether; alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, isobutyl alcohol, benzyl alcohol, and cyclohexanol; amides such as dimethylformamide, and dimethylacetamide; ketones and ketone alcohols such as acetone, and diacetone alcohol; ethers such as tetrahydrofuran, and dioxane; and nitrogen-containing heterocyclic ketones such as N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone.

The water-soluble organic solvent may be incorporated in such an amount that the ink-bleeding is not caused and the ejection property is not impaired. Among the above solvents, preferred are ethylene glycol, triethylene glycol, hexylene glycol, diethylene glycol, glycerin, ethyl alcohol, isopropyl alcohol, cyclohexanol, and so forth. The solvent preferably is contained in an amount of from 1 to 15 % by weight based on the total weight of the ink.

The dyes employed in the present invention include direct dyes, acid dyes, reactive dyes, disperse dyes, vat dyes, and the like. The content of the dye is decided depending on the kinds of the liquid medium components and the required properties of the ink, and is generally in the range of from 0.5 to 15 %, preferably from 1 to 7 % by wight based on the total weight of the ink.

The main constituents of the ink of the present first invention are described above. Other additives may be incorporated provided that the objects of the invention are achievable. The additive includes viscosity-adjusting agents such as polyvinyl alcohol, celluloses, and water-soluble resins; pH-controlling agents such as diethanolamine, triethanolamine, and buffer solutions; fungicides; and so forth. To the ink of electrically chargeable type used for ink-jet recording in which the ink droplets are charged, a resistivity-adjusting agent

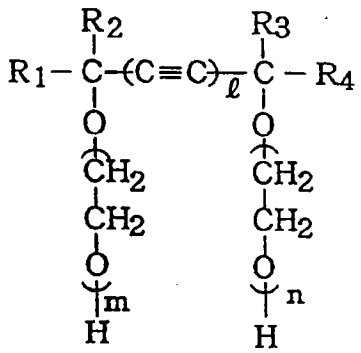
is added such as lithium chloride, ammonium chloride, and sodium chloride.

The second invention will be described in detail.

Generally, inks which contain a compound having one triple bond in the molecule give uniform color. However, the ink of the present second invention provides much more excellent uniformity of color than the above ink containing a compound having one triple bond.

Presumably, the compound which is represented by General Formula [5] having two or more triple bonds and contained in the ink of the present second invention has high electron density in the molecule and has rigid hydrophobic portion (triple bond-containing portion), causing little a free change in structure in comparison with the compound having one triple bond, whereby the compound of General Formula [5] orients regularly to the surface of the ink, and interacts effectively with the recording medium at the interface to exhibit high wettability.

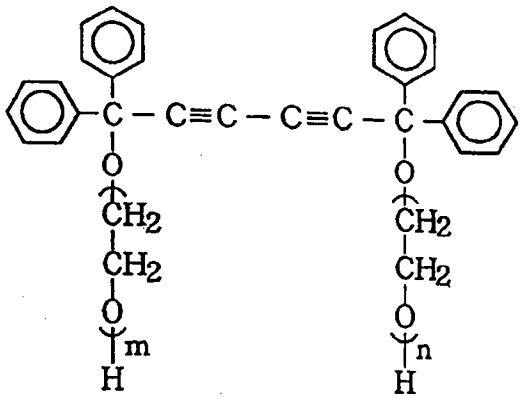
The ink of the present second invention contains the compound of General Formula [5] below in an amount of preferably from 0.001 to 20 %, more preferably from 0.001 to 5 % by weight based on the total weight of the ink, and the number of m + n in the formula is in the range of from 0 to 50.



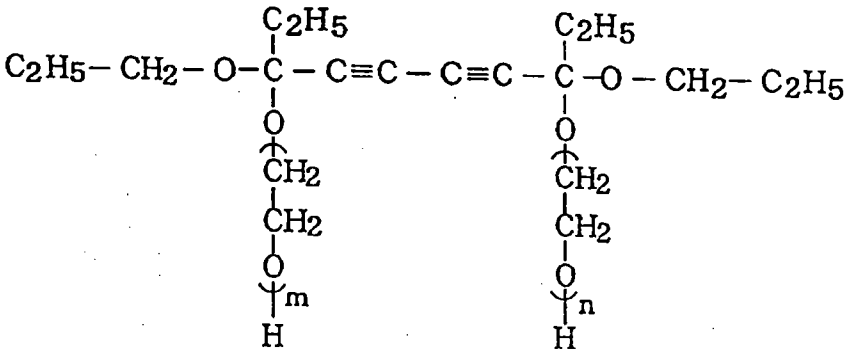
[5]

Specific examples of the compound of General Formula [5] are shown below without limiting the compound thereto in any way.

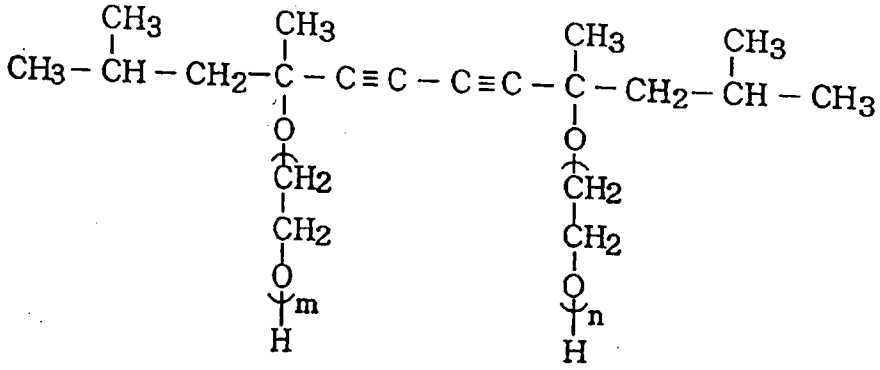
No.1



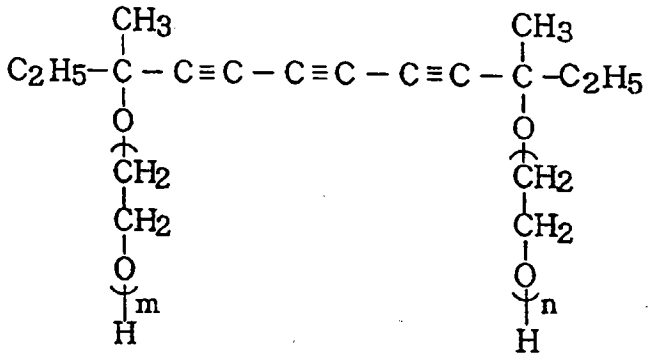
No.2



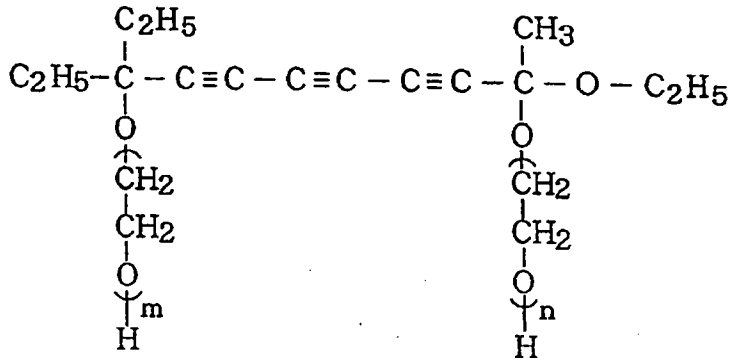
No.3



No.4



No.5



The liquid medium constituting the ink of the present second invention may be an plain water-soluble organic solvent. The water-soluble solvents include polyalkylene glycols such as polyethylene glycol, and polypropylene glycol; alkylene glycols having 2 to 6 carbon atoms such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, hexylene glycol, diethylene glycol, and thiodiglycol; glycerin; 1,2,6-hexanetriol; lower alkyl ether of polyhydric alcohols such as ethylene glycol methyl ether, diethylene glycol methyl (or ethyl) ether, and triethylene glycol monomethyl (or ethyl) ether; alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, isobutyl alcohol, benzyl alcohol, and cyclohexanol; amides such as dimethylformamide, and dimethylacetamide; ketones and ketone alcohols such as acetone, and diacetone alcohol; ethers such as

tetrahydrofuran, and dioxane; and nitrogen-containing heterocyclic ketones such as N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone.

Among the above water-soluble solvents, preferred are ethylene glycol, triethylene glycol, hexylene glycol, diethylene glycol, glycerin, thiodiglycol, ethyl alcohol, isopropyl alcohol, cyclohexanol, and so forth. The solvent is preferably contained at a content of from 1 to 35 % based on the total weight of the ink.

The dyes employed in the present invention include direct dyes, acid dyes, basic dyes, reactive dyes, disperse dyes, vat dyes, and the like. The content of the dye is decided depending on the kinds of the liquid medium components and the required properties of the ink, and is generally in the range of from 0.5 to 15 %, preferably from 1 to 7 % by weight based on the total weight of the ink.

The main constituents of the ink of the present second invention are described above. Other additives may be added provided that the objects of the invention are achievable. The additives include clogging-preventing agents such as urea and its derivatives; viscosity-adjusting agents such as polyvinyl alcohol, celluloses, and water-soluble resins; pH-controlling agents such as diethanolamine, triethanolamine, and buffer solutions; fungicides; surfactants, and so forth. To the ink of electrically chargeable type used for ink-jet recording in which the ink droplets are charged, an resistivity-adjusting agent is preferably incorporated such as lithium chloride, ammonium chloride, and sodium chloride.

The inks of the first invention and the second invention are suitable for ink-jet recording in which the ink droplets are ejected by action of thermal energy. However, the inks are naturally useful also for other types of ink-jet recording and for general writing implements.

The recording apparatus suitable for recording with the ink of the present first invention and the present second invention includes those in which thermal energy is given to the ink in a chamber in a recording-head in correspondence with recording signals and thereby ink droplets are formed.

The third invention will be described in detail.

The inventors of the present invention have noticed the necessary conditions shown below for forming color images in high quality on plain paper.

When different color inks are dotted in a pattern as shown in Fig. 1, the different color inks are less liable to be mixed at the boundaries of the dotted colors, even if the adjacent color is dotted subsequently in a short time. In this case, however, disadvantages may be caused such that the central portion surrounded by dots becomes blank, which may cause decrease of color density, and a slight shift of the ejected ink droplet from the aimed impact point may increase the area of the blank portion.

On the contrary, if the ink is dotted as shown in Fig. 2 by satisfying the Equation [II] below, the above disadvantage is significantly reduced, and excellent images are obtained:

$$B \geqq \sqrt{2} \times 10^3 \times 1/D \qquad [II]$$

where B is a dot diameter (μm) formed on plain paper, and D is a recording density (dots/mm). In this method of dotting, however, different color inks are necessarily mixed as shown by the shadowed portions in Fig. 2, and thereby mixing of the different color inks is liable to occur.

In Figs. 1 and 2, C, M and Y means a droplet of cyan ink, magenta ink and yellow ink, respectively.

The inventors have investigated the method of preventing the mixing of different color inks at the color boundaries with the high quality of image being maintained regarding the case where the inks are dotted according to Equation [II]. As the result, it has been found that the above problem is solved by adjusting the feathering rate (A) shown by Equation [I] below on plain paper to be in the range of from 2.5 to 3.5.

$$A = B/C \qquad [I]$$

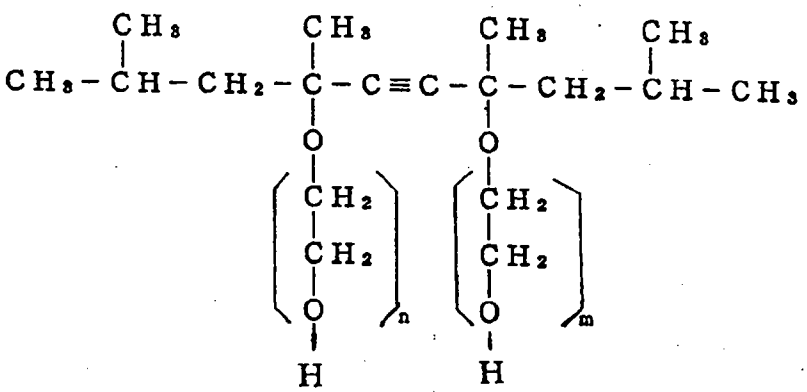
where B is a dot diameter (μm) formed on plain paper, and C is a diameter (μm) of the ejected ink droplet. At the feathering rate of less than 2.5,
the ink droplet attached on paper surface spreads less and the ink layer does not become thin, thereby different colors of inks coming to be mixed at the boundaries of colors when inks are dotted under the conditions shown in Fig. 2. On the contrary, at the feathering rate of more than 3.5, the ink droplet spreads excessively and the edge of the dot becomes unclear, thus providing images of low quality.

In order to control the feathering ratio in the range of from 2.5 to 3.5, nonionic surfactant is incorporated into the ink in an amount of from 1 to 20 %, more preferably from 3 to 10 % by weight. With the amount of the nonionic surfactant of less than 1 % by weight, the feathering ratio becomes less than 2.5, thus causing color ink mixing at the color border, while with the amount of the nonionic surfactant of more than 20 % by weight, the feathering rate becomes more than 3.5, thus the image quality liable to become low.

Simple use of surfactant in a large amount gives rise to disadvantages of lowering of color density and image quality caused by excessive penetration of ink droplets toward the back face of the paper sheet, and of nonuniformity of color density in a solid print portion caused by nonuniform dyeing of the fiber layer at the paper surface. The inventors of the present invention have found that color image recording with high quality is practicable when a nonionic surfactant is used as the surfactant and when printing is carried out using the ink containing it in an amount of from 1 to 20 % by weight with controlling the amount of ink ejection in the range of from 10 to 70 pℓ, preferably from 20 to 50 pℓ per one nozzle for one pulse. The present third invention has been accomplished on the basis of the above two findings.

The nonionic surfactant does not have selective affinity to a fiber layer on the surface of paper, whereby uniform dyeing is achievable and nonuniformity of color density is avoided. The ink for the color recording method of the present invention contains a surfactant in a large amount. Therefore, if the ink droplets are ejected in an amount of more than 70 pℓ per one nozzle for one pulse, the amount of the ink exceeds the absorbable and fixable limit of the fiber layer on the paper surface, causing penetration of ink into a pore layer under the fiber layer owing to the penetrating power of the surfactant, thus resulting in deterioration of image quality owing to lowered color density and irregular feathering. Accordingly the amount of the ink ejection has to be controlled to be in the range of from 10 to 70 pℓ per pulse.

The nonionic surfactants employed in the present third invention include polyoxyethylene alkyl ethers, polyoxyethylene phenyl ethers, polyoxyethylene-polyoxypropylene glycols, polyoxyethylene-polyoxypropylene alkyl ethers, polyethylene oxide adducts of acetylene glycol, etc. Of these, preferred are nonylphenyl ether-ethylene oxide adducts, ethylene oxide-propylene oxide copolymer (EO-PO adducts), acetylene glycol-polyethylene oxide adducts;
particularly preferred are acetylene glycol-polyethylene oxide adducts (acetylene glycol-EO adducts) represented by the structural formula below.



where m + n = 10.

The water-soluble organic solvents employed in addition to the nonionic surfactant in the present third invention include amides such as dimethylformamide, and dimethylacetamide; ketones such as acetone; ethers such as tetrahydrofuran, and dioxane; polyalkylene glycols such as polyethylene glycol, and polypropylene glycol; alkylene glycols having 2 to 6 carbon atoms such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, thiodiglycol, hexylene glycol, and diethylene glycol; glycerin; 1,2,6-hexanetriol; lower alkyl ether of polyhydric alcohols such as ethylene glycol methyl (or ethyl) ether, diethylene glycol methyl (or ethyl) ether, and triethylene glycol monomethyl (or ethyl) ether; N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, triethanolamine, sulfolane, dimethylsulfoxide, and so forth.

The clogging-preventing agents include urea and derivatives of urea, sulfonamides, and the like.

The dyes employed in the present invention include direct dyes, acid dyes, reactive dyes, disperse dyes, vat dyes, and the like. The content of the dye is decided depending on kinds of the liquid medium components and the required properties of the ink, and is generally in the range of from 0.5 to 15 %, preferably from 1 to 7 % by weight based on the total weight of the ink.

The main constituents of the ink of the present third invention are described above. Other additives may be added provided that the objects of the invention are achievable. The additives include viscosity-adjusting agents such as polyvinyl alcohol, celluloses, and water-soluble resins; pH-controlling agents such as diethanolamine, triethanolamine, and buffer solutions; fungicides; and so forth. To formulate the ink of electrically chargeable type used for ink-jet recording in which the ink droplets are charged, an resistivity-

adjusting agent is preferably added such as lithium chloride, ammonium chloride, and sodium chloride.

The recording method of the present third invention is particularly suitable for ink-jet recording in which ink droplets are ejected by the action of thermal energy, but is also applicable to other ink-jet recording methods.

A recording apparatus is described below which produces ink droplets by thermal energy and is suitable for practising the recording of the present first invention, the present second invention, and the present third invention. The present invention is suitable for the recording system in which recording signal is applied to a recording ink in a recording head and ink droplets are ejected by the action of the generated thermal energy. The construction of the recording head, which is the main portion of the apparatus, is shown in Figs. 3, 4, and 5.

A head 13 is constructed by bonding a plate of glass, ceramics, or plastics having an ink flow path to a heat-generating head 15. (The the head is shown in the drawing, but the invention is not limited to this.) The heat-generating head 15 is constituted of a protection layer 16 formed of silicon oxide or the like, aluminum electrodes 17-1 and 17-2, a heat-generating resistance layer 18 formed of nichrome or the like, a heat accumulation layer 19, and a substrate plate 20 made of aluminum or the like having a high heat-radiating property.

Ink 21 reaches the ejection orifice 22, forming a meniscus 23 by action of pressure P not shown in the drawing.

On application of an electric signal to the electrodes 17-1 and 17-2, the region designated by a symbol "n" on the heat-generating head 15 generates abruptly heat to form a bubble in the portion of the ink 21 contacting therewith. The pressure generated by the bubble pushes out the meniscus 23 and ejects the ink 21 from the orifice 22 in a form of ink droplets 24, and the ink droplets are ejected to a recording medium 25. Fig. 5 shows a rough sketch of a multiple recording head constructed by juxtaposing a multiplicity of heads shown in Fig. 3. The recording head is prepared by bonding a glass plate 27 having a plurality of flow paths to a heat-generating head 28 similar to the one shown in Fig. 3.

Incidentally, Fig. 3 is a cross-sectional view of the head 13 along an ink flow path, and Fig. 4 is a cross-sectional view of the head at the line A-B in Fig. 3.

Fig. 6 illustrates an example of the ink-jet recording apparatus having such a head mounted therein.

In Fig. 6, a blade 61 as a wiping member is held at one end by a blade-holding member, forming a fixed end in a shape of a cantilever. The blade 61 is placed at a position adjacent to the recording region of the recording head, and is constituted such that it moves in the direction perpendicular to the moving direction of the recording head to come into contact with the ejection nozzle face to cap the nozzles. An ink absorption member 63 is provided at a position adjacent to the blade 61, and is held so as to protrude into the moving path of the recording head in a manner similar to that of the blade 61. The aforementioned blade 61, the cap 62, and the absorption member 63 constitute an ejection-recovery section 64. The blade 61 and the absorption member 63 remove water, dust, and the like from the ink ejecting nozzle face.

A recording head 65 has an ejection energy-generating means for ejection, and conducts recording by ejecting ink onto a recording medium opposing to the ejection nozzle face. A carriage 66 is provided for supporting and moving the recording head 65. The carriage 66 is engaged slideably with a guide rod 67. A portion of the carriage 66 is connected (not shown in the drawing) to a belt 69 driven by a motor 68, so that the carriage 66 is movable along the guide rod 67 to the recording region of the recording head 65 and the adjacent region thereto.

A paper delivery portion 51 for delivery of a recording medium and a paper delivery roller 52 driven by a motor (not shown in the drawing) delivers the recording medium to the position opposing to the ejecting nozzle face of the recording head, and the recording medium is discharged with the progress of the recording to a paper discharge portion provided with paper-discharging rollers 53.

In the above constitution, when the recording head 65 returns to a home position at the completion of the recording or other timing, the cap 62 of the ejection-recovery portion 64 is positioned out of the moving path of the recording head 65, and the blade 61 is made to protrude into the moving path. Therefore, the ejecting nozzle face of the recording head 65 is wiped therewith. The cap 62 moves to protrude toward the moving path of the recording head when the cap 62 comes into contact with the ejecting nozzle face of the recording head for capping.

At the time when the recording head 65 moves from the home position to the record-starting position, the cap 62 and the blade 61 are at the same position as in the above-mentioned wiping time, so that the ejection nozzle face of the recording head is wiped also in this movement.

The recording head moves to the home position not only at the end of the recording and at the time of ejection recovery, but also at a predetermined interval during movement for recording in the recording region. By such movement, the wiping is conducted.

Fig. 7 illustrates an example of the ink cartridge that contains ink to be supplied through an ink supplying member such as a tube. The ink container portion 40, for example an ink bag, contains an ink to be supplied, and has a rubber plug 42 at the tip. By inserting a needle (not shown in the drawing) into the plug 42, the ink in the ink bag 40 becomes suppliable. An ink absorption member 44 absorbs waste ink.

The ink container portion has preferably a liquid-contacting surface made of polyolefin, particularly preferably made of polyethylene.

The ink-jet recording apparatus used in the present invention is not limited to the above-mentioned one which has separately a head and an ink cartridge. Integration thereof as shown in Fig. 8 may suitably be used.

In Fig. 8, a recording unit 70 houses an ink container portion such as an ink absorption member, and the ink in the ink absorption member is ejected from a head 71 having a plurality of orifices. The ink absorption member may be made of a material such as polyurethane. An air-communication opening 72 is provided to communicate interior of the cartridge with the open air. The recording unit 70 may be used in place of the recording head shown in Fig. 6, and is readily mountable to and demountable from the carriage 66.

An ink-jet recording apparatus which ejects ink droplets by action of thermal energy to the ink is exemplified above. The present invention, however, is applicable also to other ink-jet recording apparatuses such as the one of piezo type which employs a piezoelectric element.

For practising the recording according to the present invention, a recording apparatus, for example, is used which has four in number of recording heads shown in Fig. 5 juxtaposed on a carriage. Fig. 9 shows an example of the apparatus. Recording heads 81, 82, 83, and 84 are recording heads ejecting respectively recording inks of yellow, magenta, cyan, and black. The heads are mounted on the aforementioned recording apparatus, and eject respective color inks in accordance with recording signals. The apparatus in Fig. 9 employs four recording heads, but the present invention is not limited thereto. One recording head may be constructed to ejects all of the yellow, magenta, cyan, and black inks as shown in Fig. 10.

The present invention is described in more detail by reference to Examples and Comparative Examples. In the description, the terms "parts" and "%" are based on weight unless otherwise mentioned. Hereinafter, the ethylene oxide adduct is simply referred to as "EO adduct".

The dyes and liquid medium in an amount (parts) shown below are employed in the Example and Comparative Example to provide each 100 parts of inks, respectively.

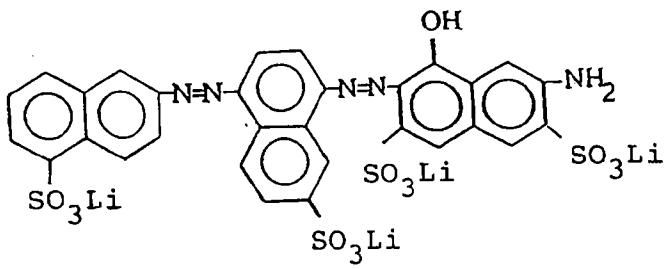
Example 1

(Dyes)		
Black:	C.I. Food Black 2	2 parts
	Dye A of Formula below	1.2 parts
	Dye B of Formula below	0.8 part
Yellow:	C.I. Direct Yellow 86	2.5 parts
Cyan:	C.I. Direct Blue 199	3.5 parts
Magenta:	Dye C of Formula below	3.5 parts

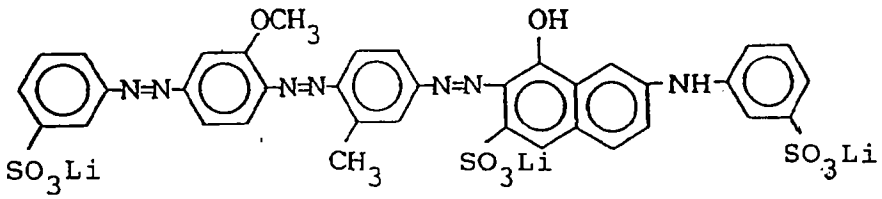
(Liquid medium)	
Thiodiglycol	7.5 parts
Urea	7.5 parts
Glycerin	7.5 parts
Higher alcohol-EO adduct (n = 15)*	1 part
Pure water	balance

* Higher alcohol-EO adduct: BO-15TX (made by Nikko Chemicals K.K.) is used.

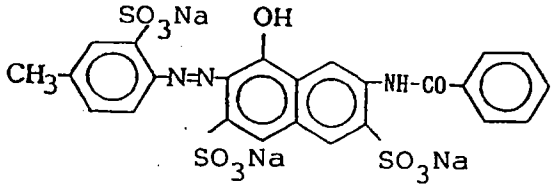
Dye A



Dye B



Dye C



Each of the four color compositions was stirred sufficiently, and was filtered under pressure through a Fluoropore Filter (trade name, made by Sumitomo Electric Industries, Ltd.) having a pore diameter of 0.22 μm to prepare the ink of the present invention. The respective inks were introduced into a color ink-jet printer BJC-820J (tarde name, made by Canon K.K.) which conducts recording by forming ink droplets by applying thermal energy to the inks in the recording heads, and recording was conducted on commercial paper sheets for copying (Canon NP Dry SK), and bond paper sheets (Plover Bond Paper PB).

Evaluation was made as described below. The results are shown in Table 1.

(1) Bleeding:

Color samples were prepared by printing such that different colors are adjacent to each other, and the occurrence of bleeding was evaluated by the standard below. The evaluation was made for seven colors: black, yellow, cyan, and magenta; and red, green, and blue formed by dotting in superposition of two colors taken from the colors of yellow, cyan, and magenta.

o : No bleeding is observed at every boundary.

△ : Bleeding is remarkable at the boundaries of red, green, and blue where a larger amount of ink is applied.

x : Bleeding is remarkable at nearly all the boundaries.

(2) Color uniformity:

Uniformity at solid color print portions are examined visually.

o : Solid color print is completely uniform without irregularity.

△ : Nonuniformity is remarkable at the portion where fiber density is high.

x : Color irregularity is much more remarkable.

(3) Occurrence of feathering:

Three hundred dots are printed continuously on a commercial paper sheet for copying and a commercial bond paper sheet such that the dots are not brought into contact with each other. The dotted ink are dried in the air for 24 hours at room temperature. Irregular shape and irregular feathering of dots are counted under microscope. The evaluation is made by the percentage of the counted dot number according

to the standard below:
◎ : not more than 10 %
o : 11 % to 30 %
Δ : 31 % to 50 %
x : not less than 51 %

(4) Ejection property:

The ink to be tested is filled to the printer, and alphabet and numeral letters are printed continuously for 10 minutes with the printer. Thereafter, printer is left standing without capping of the nozzles. After 10 minutes of intermission of the printing, the printing is started again. The ejection property is evaluated from scratches and unsharped edges in printed letters after restarting the printing.
o : No scratch and no unsharped edge is observed from the first letter.
Δ : A part of the first letter is scratched or unsharped.
x : The first letter cannot be printed.

(5) Storage stability:

The ink is placed in an amount of 100 mℓ in a heat-resistant glass bottle, stoppered tightly, and stored in a thermostatic chamber at 60 °C. After 2 months of storage, the ink is used for printing, and evaluated.
o : No abnormality is observed.
x : Failure of discharge, or irregularity or discoloration of printed letters is observed.

(6) Anti-Clogging (crusting recovery):

The ink to be tested is filled to the printer, and alphabet and numeral letters are printed continuously for 10 minutes with the printer. Thereafter, printer is left standing without capping of the nozzles. After one month of intermission of the printing, ejection recovery operation was conducted. The evaluation was made by counting the required number of times of the ejection recovery operations for carrying out normal printing.
o : Printing is normal after 1 to 5 times of ejection recovery operation.
Δ : Printing is normal after 6 to 10 times of ejection recovery operation.
x : Printing is normal after 11 or more times of ejection recovery operation.

Examples 2 to 5

In respective Examples, the kind and the amount of the dyes used were as below:

(Dyes for Examples 2 to 4)		
Black:	C.I. Food Black 2 Dye A Dye B	2 parts 1.2 parts 0.8 part
Yellow: Cyan: Magenta:	C.I. Direct Yellow 86 C.I. Direct Blue 199 Dye C	2.5 parts 3.5 parts 3.5 parts

(Dyes for Example 5)		
Black:	C.I. Food Black 2 Dye A Dye B	2 parts 1.2 parts 0.8 part
Yellow: Cyan: Magenta:	C.I. Direct Yellow 86 C.I. Acid Blue 9 Dye C	2.5 parts 3.0 parts 3.5 parts

The liquid mediums used in respective Examples were as below:

(Liquid medium for Example 2)	
Thiodiglycol	7.5 parts
Urea	7.5 parts
Glycerin	7.5 parts
Nonylphenyl ether-EO adduct (n = 9 to 10)	5 part
Pure water	balance

(Liquid medium for Example 3)	
Thiodiglycol	7.5 parts
Thiourea	7.5 parts
Glycerin	7.5 parts
Ethylene oxide-propylene oxide copolymer (n = 10, L = 7)	15 parts
Pure water	balance

(Liquid medium for Example 4)	
Thiodiglycol	7.5 parts
Urea	7.5 parts
Glycerin	7.5 parts
Acetylene glycol-EO adduct (n + m = 10)	5 parts
Pure water	balance

(Liquid medium for Example 5)	
Thiodiglycol	7.5 parts
Urea	7.5 parts
Glycerin	7.5 parts
Acetylene glycol-EO adduct (n + m = 4)	1 parts
Pure water	balance

In the above, as acetylene glycol-EO adduct, Acetylenol (made by Kawaken Fine Chemical K.K.), as the nonylphenyl ether-EO adduct, Emulgen 909 (made by Kao Corporation), and as the ethylene oxide-propylene oxide copolymer, Karpole MH-50 (made by Asahi Denka Kogyo K.K.) are used, respectively.

The respective inks were prepared with the dye and the liquid medium shown above in the same manner as in Example 1. Printing properties, ejection properties, and the storage stability of the inks were evaluated in the same manner as in Example 1. The results are shown in Table 1.

Comparative Examples 1 to 5

In respective Comparative Examples, the kind and the amount of the dyes were are as below:

(Dyes for Comparative Examples 1 to 5)		
Black:	C.I. Food Black 2 Dye A Dye B	2 parts 1.2 parts 0.8 part
Yellow: Cyan: Magenta:	C.I. Direct Yellow 86 C.I. Direct Blue 199 Dye C	2.5 parts 3.5 parts 3.5 parts

The liquid mediums used in respective Comparative Examples were as below:

(Liquid medium for Comparative Example 1)	
Thiodiglycol	7.5 parts
Urea	7.5 parts
Glycerin	7.5 parts
Pure water	balance

(Liquid medium for Comparative Example 2)	
Thiodiglycol	15 parts
Glycerin	7.5 parts
Acetylene glycol-EO adduct (n + m = 10)	5 parts
Pure water	balance

(Liquid medium for Comparative Example 3)	
Urea	10 parts
Glycerin	12.5 parts
Acetylene glycol-EO adduct (n + m = 10)	5 parts
Pure water	balance

(Liquid medium for Comparative Example 4)	
Thiodiglycol	7.5 parts
Urea	7.5 parts
Glycerin	7.5 parts
Anionic surfactant (Neopelex 25, made by Kao Corporation)	7 parts
Pure water	balance

(Liquid medium for Comparative Example 5)	
Thiodiglycol	7.5 parts
Urea	7.5 parts
Glycerin	7.5 parts
Cationic surfactant (Cation DDC-50, made by Sanyo Chemical Industries, Ltd.)	5 parts
Pure water	balance

The respective inks were prepared with the dye and the liquid medium shown above in the same manner as in Example 1. Printing properties, ejection properties, and the storage stability of the inks were evaluated in the same manner as in Example 1. The results are shown in Table 1.

Table 1

Evaluation item	(1)		(2)		(3)		(4)	(5)	(6)
	SK	PB	SK	PB	SK	PB			
Examples									
1	○	○	○	○	○	○	○	○	○
2	○	○	○	○	○	○	○	○	○
3	○	○	○	○	○	○	○	○	○
4	○	○	○	○	◎	◎	○	○	○
5	○	○	○	○	◎	◎	○	○	○
Comparative examples									
1	×	×	×	×	◎	◎	○	○	○
2	○	○	○	○	◎	◎	△	○	×
3	○	○	○	○	○	○	×	○	△
4	○	○	△	×	×	×	×	×	△
5	△	×	△	×	△	△	×	×	×

SK: Commercial paper for copying

PB: Plover Bond paper

Examples 6 to 10 and Comparative Example 6

The dyes of black, cyan, magenta, and yellow, and the amount thereof used in respective Examples and Comparative Example are as shown below:

(Dyes)		
Black:	C.I. Food Black 2 Dye A Dye B	2 parts 1.2 parts 0.8 part
Yellow: Cyan: Magenta:	C.I. Direct Yellow 86 C.I. Acid Blue 9 Dye C	2.5 parts 3.5 parts 3.5 parts

Example 6

Dye (black, yellow, cyan, or magenta) in an amount as shown above	
Glycerin	8 parts
Urea	5 parts
Thiodiglycol	8 parts
Compound No.1	1 part
Pure water	balance

The above ink compositions were respectively stirred sufficiently, and filtered through a Fluoropore Filter (pore diameter 0.22 μm, trade name, made by Sumitomo Electric Industries, Ltd.) to prepare inks of this Example.

Example 7

Dye (black, yellow, cyan, or magenta) in an amount as shown above	
Glycerin	8 parts
Urea	5 parts
Thiodiglycol	8 parts
Compound No.2	16 part
Pure water	balance

The above ink compositions were prepared in the same manner as in Example 6 to prepare inks of this Example.

Example 8

Dye (black, yellow, cyan, or magenta) in an amount as shown above	
Glycerin	8 parts
Urea	5 parts
Thiodiglycol	8 parts
Compound No.3	0.5 part
Cyclohexanol	1 part
Pure water	balance

The above ink compositions were prepared in the same manner as in Example 6 to prepare inks of this Example.

Example 9

Dye (black, yellow, cyan, or magenta) in an amount as shown above	
Glycerin	8 parts
Urea	5 parts
Thiodiglycol	8 parts
Compound No.4	10 parts
Pure water	balance

The above ink compositions were prepared in the same manner as in Example 6 to prepare inks of this Example.

Example 10

Dye (black, yellow, cyan, or magenta) in an amount as shown above	
Glycerin	8 parts
Urea	5 parts
Thiodiglycol	8 parts
Compound No.5	5 parts
Pure water	balance

The above ink compositions were prepared in the same manner as in Example 6 to prepare inks of this Example.

Comparative Example 6

Dye (black, yellow, cyan, or magenta) in an amount as shown above	
Glycerin	5 parts
Urea	5 parts
Thiodiglycol	6 parts
Pure water	balance

The above ink compositions were prepared in the same manner as in Example 6 to prepare inks of this Comparative Example.

〈 Evaluation 〉

The obtained inks of Examples 6 to 10 and Comparative Example 6 were used for printing on commercial paper sheets for copying (Canon NP dry SK, and Prober bond paper PB). The recording apparatus employed was similar to the one shown in Fig. 6. A color image was formed by use of four recording heads shown in Fig. 9. The recording heads were the same as the ones used in the ink-jet printer BJC-820J (trade name, made by Canon K.K.). The recording heads were driven under the driving conditions (or current-flowing conditions) of the applied voltage of 28 V, the pulse width of 3.2 μsec, and the drive frequency of 5 kHz.

The inks were evaluated regarding the evaluation items below. The results are shown in Table 2.

(1) Bleeding:

Evaluated in the same manner as in Example 1.

(2) Uniformity of color:

Evaluated in the same manner as in Example 1.

(3) Rate of occurrence of feathering:

Three hundred dots are printed continuously on a commercial paper sheet for copying and a commercial bond paper sheet such that the dots are not brought into contact with each other. The dotted ink are dried in the air for 24 hours at room temperature. Irregular shape and irregular feathering of dots are counted under microscope. The evaluation is made by the percentage of the counted dot number according to the standard below:

o : not more than 10 %
Δ : 10 % to 20 %
x : not less than 21 %

(4) Storage stability:

Evaluated in the same manner as in Example 1.

(5) Anti-Clogging (crusting recovery):

Evaluated in the same manner as in Example 1.

Table 2

Evaluation item	(1)	(2)	(3)	(4)	(5)
Example 6	o	o	o	o	o
Example 7	o	o	o	o	o
Example 8	o	o	o	o	o
Example 9	o	o	o	o	o
Example 10	o	o	o	o	o
Comparative example 6	x	x	o	o	o

Examples 11 to 18 and Comparative Examples 7 to 10

A color ink-jet recording apparatus which has four heads of the same recording density for yellow, magenta, cyan, and black colors and conducts recording by generation of ink droplets upon applying thermal energy to the inks in the recording head was employed. Three kinds of multiple-nozzle On-Demand type heads of recording densities of 300 dpi (11.8 dots/mm), 360 dpi (14.2 dots/mm), and 400 dpi (15.7 dots/mm) were used.

The color inks (yellow, magenta, cyan, and black) for respective Examples were prepared by stirring sufficiently the composition shown below and filtering the mixture through Fluoropore Filter (pore diameter of 0.22 μm, trade name, made by Sumitomo Electric Industries, Ltd.) under pressure.

(Dyes)		
Black:	C.I. Food Black 2 Dye A Dye B	2 parts 1.2 parts 0.8 part
Yellow: Cyan: Magenta:	C.I. Direct Yellow 86 C.I. Direct Blue 199 Dye C	2.5 parts 3.5 parts 3.5 parts

(Liquid medium)	
Thiodiglycol	7.5 parts
Urea	7.5 parts
Glycerin	7.5 parts
Surfactant	(as shown in Table 3)
Pure water	balance

With the recording apparatus having the heads of recording density shown in Table 3 mounted thereon, recording was conducted at the ejection rate shown on commercial paper for copying (Canon NP dry SK, and Xerox 4024), and commercial bond paper (Plover bond paper sheet PB), and the recorded matter was evaluated.

The printed dot diameters and the feathering rates derived from the dot diameter are shown in Table 3. The evaluation results are shown in Table 4.

Recording was carried out under environmental conditions of the temperature of 25±2°C and the humidity of from 50 to 70 % RH, and the printed samples were evaluated after they were left for one day from the time they were printed.

The dot diameter ("B" in Equation [I]) in the present invention was derived by image processing of printed dots by means of a CCD camera to measure the area of the dot and conversion of the area to a diameter of precise circle. The ink droplet diameter ("C" in Equation [I]) was calculated from the equation below:

$$V = (4/3)\pi(C/2)^3 \times 10^{-3}$$

where V is the volume of a droplet (pℓ) ejected per one pulse.

The evaluation items:

(1) Bleeding,

(2) Uniformity of color, and

(3) rate of feathering

were evaluated in the same manner as in Example 1.

(4) Optical density:

The optical density of the printed matter was measured by MacBeth Refractodensitometer RD-915 (made by MacBeth Co.). The average O.D. values of yellow, magenta, cyan, and black were evaluated according to the standard below:

o : not less than 1.0

Δ : 0.9 to 1.0

x : not more than 0.9

Table 3

	Surfactant		Recording density	Dot diameter (B)	Ink-drop diameter (C)	Amount of ejection	Ink-running rate (A)
	Type	Concentration (parts)	(dots/mm)	(μm)	(μm)	(pℓ)	
Example							
11	Acetylene glycol-EO adduct	1.5	14.2	114.4	44	44.6	2.6
12	Acetylene glycol-EO adduct	5	14.2	123.2	44	44.6	2.8
13	Acetylene glycol-EO adduct	15	14.2	136.4	44	44.6	3.1
14	Acetylene glycol-EO adduct	15	15.7	91.8	27	10	3.4
15	Acetylene glycol-EO adduct	10	14.2	116.5	38.5	30	2.9
16	Acetylene glycol-EO adduct	5	11.8	131.0	48.5	60	2.7
17	EO-PO copolymer	7	15.7	97.2	36	24.4	2.7
18	Nonylphenyl ether-EO adduct	5	11.8	130.5	45	47.7	2.9
Comparative Example							
7	Acetylene glycol-EO adduct	0.5	14.2	101.2	44	44.6	2.3
8	Acetylene glycol-EO adduct	5	11.8	143.1	53	78.0	2.7
9	Acetylene glycol-EO adduct	2.5	14.2	162.8	44	44.6	3.7
10	Sodium dodecylbenzenesulfonate	5	15.7	98.1	44	44.6	2.2

Table 4

		Bleeding	Feathering	Optical density	Density irregularity
Example	11	Δ	○	○	○
	12	○	○	○	○
	13	○	Δ	○	○
	14	○	○	Δ	○
	15	○	○	○	○
	16	○	Δ	○	○
	17	○	○	○	○
	18	○	○	○	○
Comparative Example	7	×	×	Δ	Δ
	8	○	×	×	○
	9	○	×	×	○
	10	×	×	×	×

As described above, the present invention gives color images of high quality formed by dots of precisely circle shape with excellent color density without causing feathering, bleeding, and color nonuniformity even on plain paper.

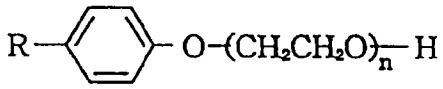
Furthermore, the present invention enables excellent recording without failure of ejection after intermission of printing with stability and without nozzle clogging.

Provided is an ink for ink-jet recording, comprising a dye, water, and the components (a), (b), and (c) below:

(a) at least one surfactant selected from the group consisting of higher alcohol-ethylene oxide adducts represented by General Formula [1], alkylphenol-ethylene oxide adducts represented by General Formula [2], ethylene oxide-propylene oxide copolymers represented by General Formula [3], and acetylene glycol-ethylene oxide adducts represented by General Formula [4], at a content of from 0.1 to 20 % by weight;

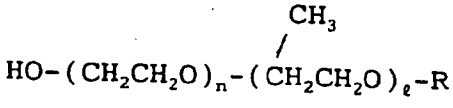
$R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}H$ [1]

where R is alkyl, and n is an integer;



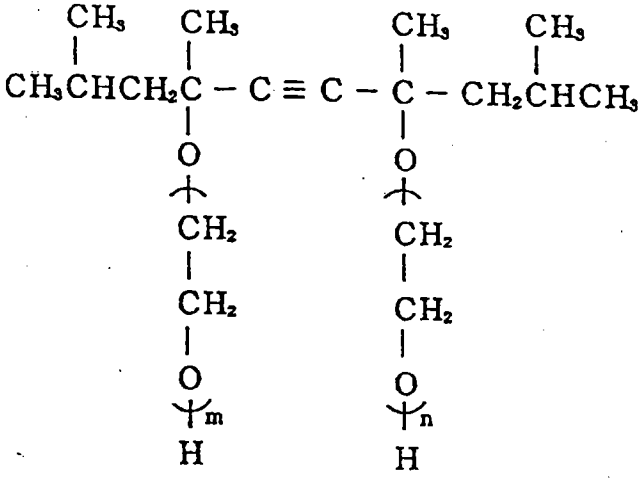
[2]

where R is alkyl, and n is an integer;



[3]

where R is alkyl, and n and ℓ are respectively an integer;



[4]

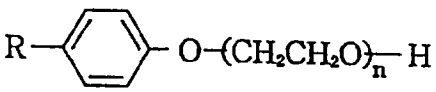
where m and n are respectively an integer;
(b) thiodiglycol; and
(c) urea or an derivative thereof.

Claims

1. An ink for ink-jet recording, comprising a dye, water, and the components (a), (b), and (c) below:
(a) at least one surfactant selected from the group consisting of higher alcohol-ethylene oxide adducts represented by General Formula [1], alkylphenolethylene oxide adducts represented by General Formula [2], ethylene oxide-propylene oxide copolymers represented by General Formula [3], and acetylene glycol-ethylene oxide adducts represented by General Formula [4], at a content of from 0.1 to 20 % by weight;

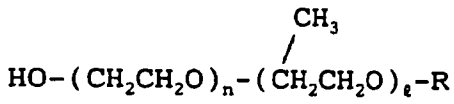
$R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}H$ [1]

where R is alkyl, and n is an integer;



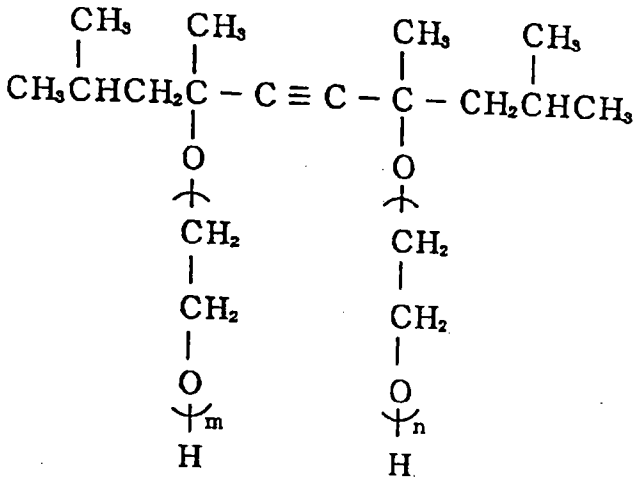
[2]

where R is alkyl, and n is an integer;



[3]

where R is alkyl, and n and ℓ are respectively an integer;



[4]

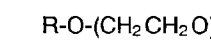
where m and n are respectively an integer;
(b) thiodiglycol; and
(c) urea or an derivative thereof.

2. An ink for ink-jet recording according to Claim 1, wherein the ink contains thiodiglycol at a content of from 1 to 30 % by weight.

3. An ink for ink-jet recording according to Claim 1, wherein the ink contains urea or the derivative thereof at a content of from 1 to 30 % by weight.

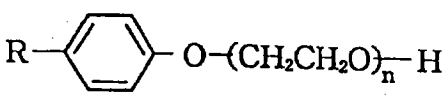
4. An ink for ink-jet recording according to Claim 1, wherein the value of n or n + m in General Formulas [1] to [4] is from 4 to 20.

5. An ink-jet recording method of conducting recording on a recording medium with ink droplets of ink, said ink comprising a dye, water, and the components (a), (b), and (c):
(a) at least one surfactant selected from the group consisting of higher alcohol-ethylene oxide adducts represented by General Formula [1], alkylphenol-ethylene oxide adducts represented by General Formula [2], ethylene oxide-propylene oxide copolymers represented by General Formula [3], and acetylene glycol-ethylene oxide adducts represented by General Formula [4], at a content of from 0.1 to 20 % by weight;



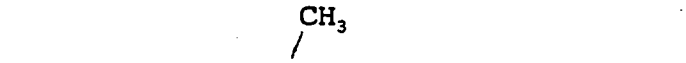
[1]

where R is alkyl, and n is an integer;



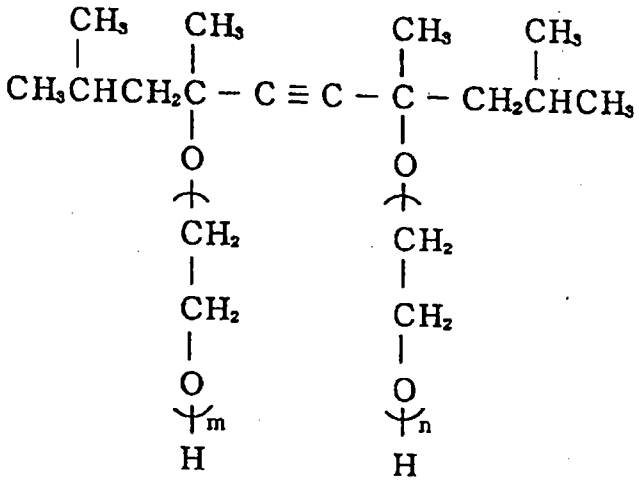
[2]

where R is alkyl, and n is an integer;



[3]

where R is alkyl, and n and ℓ are respectively an integer;



[4]

where m and n are respectively an integer;

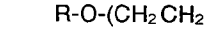
(b) thiodiglycol; and

(c) urea or an derivative thereof.

6. An ink-jet recording method according to Claim 5, wherein ink droplets are ejected by action of thermal energy applied to the ink.

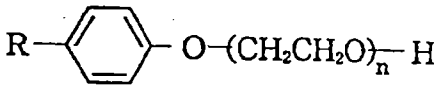
7. A color ink-jet recording method of conducting recording by ejecting droplets of ink of two or more colors onto adjacent or superposed positions on a recording medium, said ink comprises a dye, water and the components (a), (b), and (c):

(a) at least one surfactant selected from the group consisting of higher alcohol-ethylene oxide adducts represented by General Formula [1], alkylphenol-ethylene oxide adducts represented by General Formula [2], ethylene oxide-propylene oxide copolymers represented by General Formula [3], and acetylene glycol-ethylene oxide adducts represented by General Formula [4], at a content of from 0.1 to 20 % by weight;



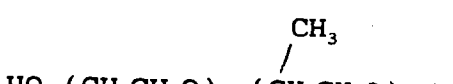
[1]

where R is alkyl, and n is an integer;



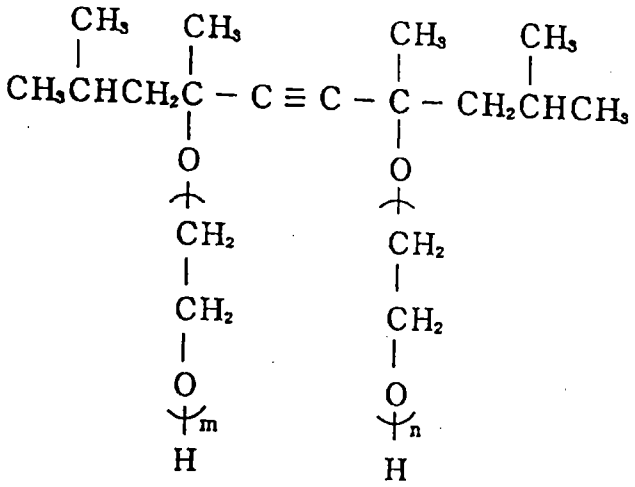
[2]

where R is alkyl, and n is an integer;



[3]

where R is alkyl, and n and ℓ are respectively an integer;

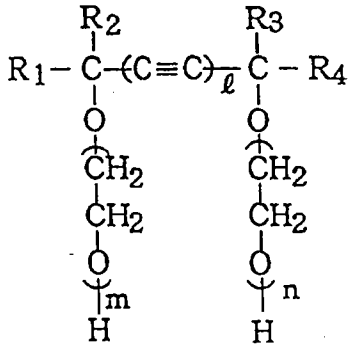


[4]

where m and n are respectively an integer;
(b) thiodiglycol; and
(c) urea or an derivative thereof.

8. A color ink-jet recording method according to Claim 7, wherein ink droplets are ejected by action of thermal energy applied to the ink.

9. An ink containing at least a dye, a water-soluble organic solvent, and water: said ink comprises further a compound of the formula



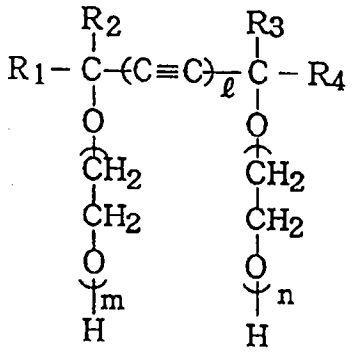
[5]

where R_1, R_2, R_3, and R_4 are respectively hydrogen, an alkyl or alkenyl group of 1 to 4 carbon atoms, or a substituted or unsubstituted phenyl group; and m + n is ranging from 0 to 50; and ℓ is a number of 2 or more.

10. An ink according to Claim 9, wherein the ink contains the compound represented by General Formula [5] at a content of from 0.001 % to 20 % by weight.

11. An ink according to Claim 9, wherein the water-soluble organic solvent is selected from the group consisting of polyhydric alcohols, monohydric alcohols, and derivatives thereof.

12. An ink-jet recording method of conducting recording with droplets of ink on a recording medium, said ink comprises a dye, a water-soluble organic solvent, water, and a compound of the formula

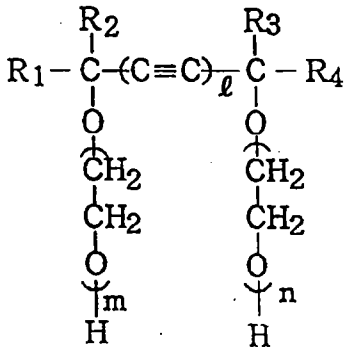


[5]

where R_1, R_2, R_3, and R_4 are respectively hydrogen, an alkyl or alkenyl group of 1 to 4 carbon atoms, or a substituted or unsubstituted phenyl group; and m + n is ranging from 0 to 50; and ℓ is a number of 2 or more.

13. An ink-jet recording method according to Claim 12, wherein ink droplets are ejected by action of thermal energy applied to the ink.

14. A color ink-jet recording method of conducting recording by ejecting droplets of ink of two or more colors onto adjacent or superposed positions on a recording medium, said ink comprises a dye, a water-soluble organic solvent, water, and the compound of the formula



[5]

where R_1, R_2, R_3, and R_4 are respectively hydrogen, an alkyl or alkenyl group of 1 to 4 carbon atoms, or a substituted or unsubstituted phenyl group; and m + n is ranging from 0 to 50; and ℓ is a number of 2 or more.

15. A color ink-jet recording method according to Claim 14, wherein ink droplets are ejected by action of thermal energy applied to the ink.

16. An ink-jet recording method according to any of Claims 5, 7, 12, and 14, wherein the recording medium has fiber exposed on the surface thereof.

17. A recording unit having an ink container portion for holding ink, and a head portion for ejecting the ink as ink droplets, said ink is as defined in Claim 1 or 9.

18. A recording unit according to Claim 17, wherein the head portion comprises a head which ejects ink droplets by action of thermal energy applied to the ink.

19. An ink cartridge comprising an ink container portion for holding ink, said ink is as defined in Claim 1 or Claim 9.

20. An ink cartridge according to Claim 19, wherein the ink container portion is in a bag-shape structure.

21. An ink cartridge according to Claim 19, wherein the ink container portion has a liquid-contacting face formed of polyolefin.

22. An ink-jet recording apparatus comprising the recording unit of Claim 16, wherein the ink defined in Claim 1 or Claim 9 is employed.

23. An ink-jet recording apparatus according to Claim 22, wherein the recording unit comprises a carriage.

24. An ink-jet recording apparatus, comprising an ink cartridge of Claim 19 and a recording head.

25. An ink-jet recording apparatus of Claim 24, the apparatus further comprises an ink supplying system for supplying ink from the ink cartridge to the recording head.

26. A color ink-jet recording method in which droplets of two or more color inks are ejected in accordance of pulse signals onto adjacent or superposed positions on a recording medium, said ink comprises a nonionic surfactant in an amount of from 1.0 to 20.0 % by weight, the ink ejected for one pulse is in an amount of from 10 to 70 pℓ, and the feathering rate (A) defined by Equation [I] is in the range of from 2.5 to 3.5:

$$A = B/C \quad [I]$$

where B is a diameter (μm) of a dot formed on plain paper, and C is a diameter (μm) of the ejected ink droplet.

27. A color ink-jet recording method according to Claim 26, wherein the nonionic surfactant contains at least one selected from polyoxyethylene alkyl ether, polyoxyethylene phenyl ether, polyoxyethylene-polyoxypropylene glycol, polyoxyethylene-polyoxypropylene alkyl ether, and acetylene glycol-polyethylene oxide adducts.

28. A color ink-jet recording method according to Claim 26, wherein the recording medium has fiber exposed on the surface thereof.

29. An color ink-jet recording apparatus which conducts recording by ejecting droplets of two or more color inks onto adjacent or superposed positions on a recording medium, said apparatus comprises a recording means for conducting recording mode, by use of an ink containing a nonionic surfactant in an amount of from 1.0 to 20.0 % by weight, by ejecting the ink for one pulse in an amount of from 10 to 70 pℓ to form ink dots at the feathering rate (A) defined by Equation [I] is in the range of from 2.5 to 3.5:

$$A = B/C \quad [I]$$

where B is a diameter (μm) of a dot formed on plain paper, and C is a diameter (μm) of the ejected ink droplet.

FIG. 1

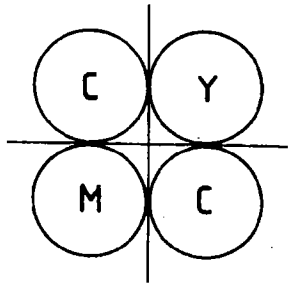


FIG. 2

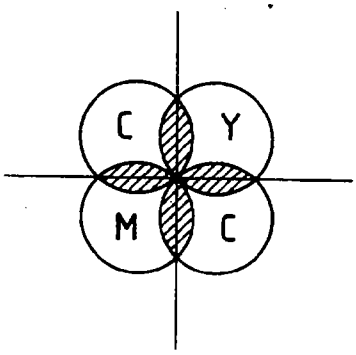


FIG. 3

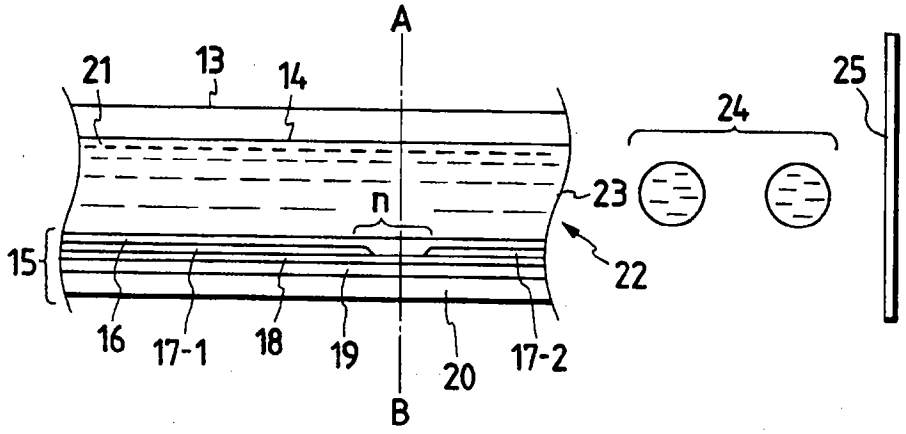


FIG. 4

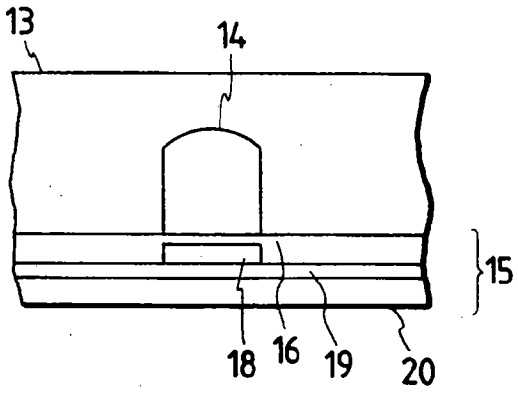
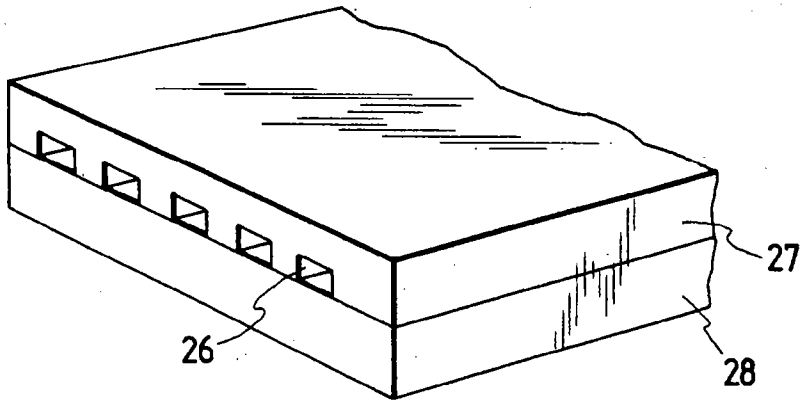


FIG. 5



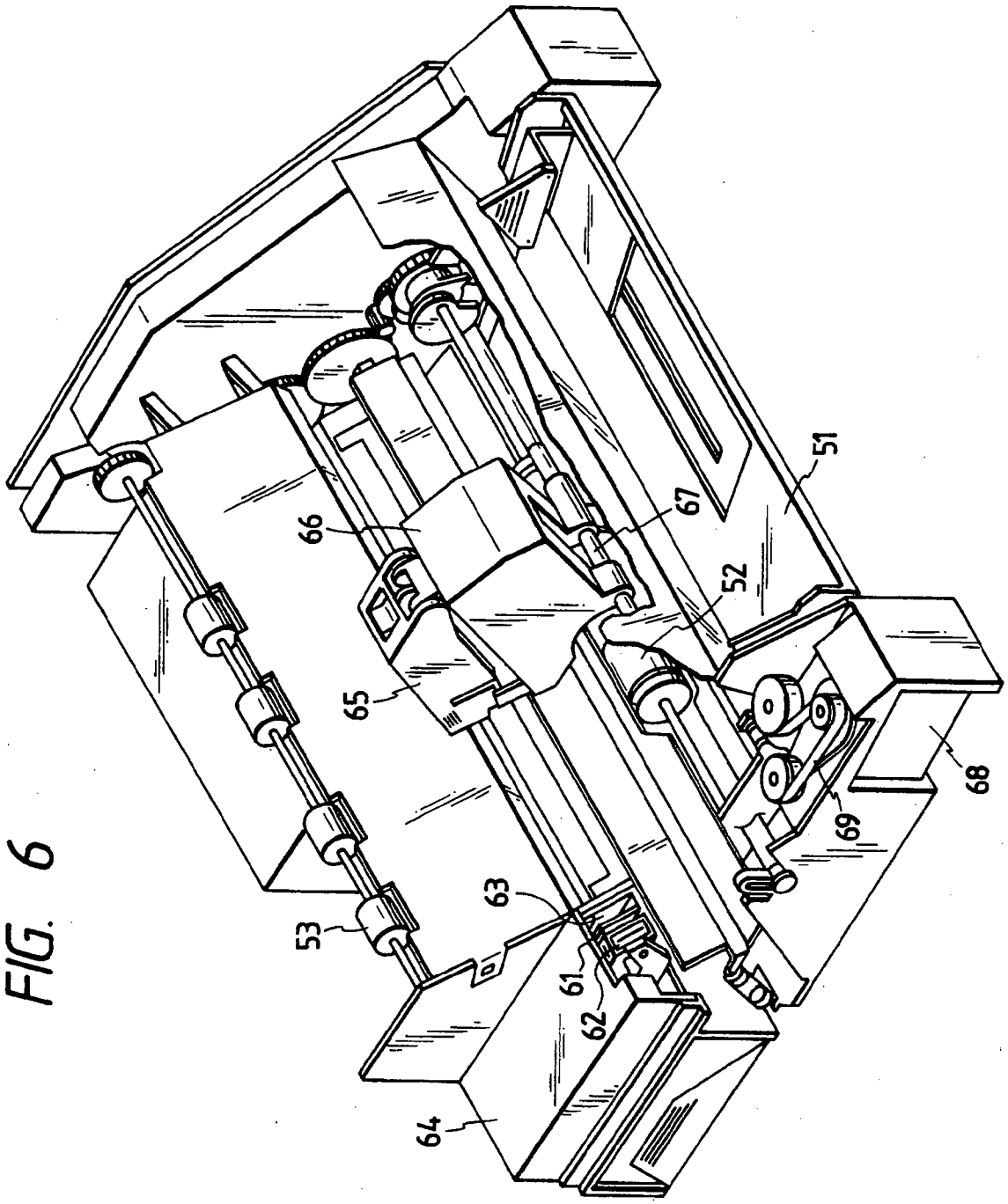


FIG. 6

FIG. 7

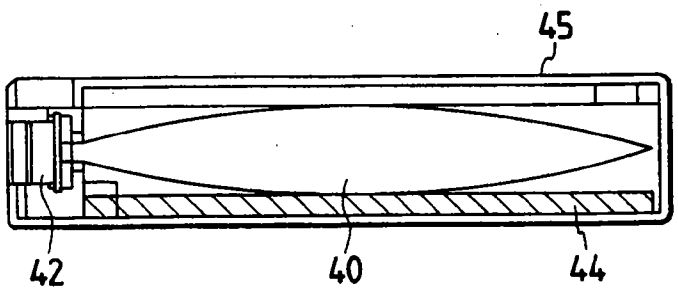


FIG. 8

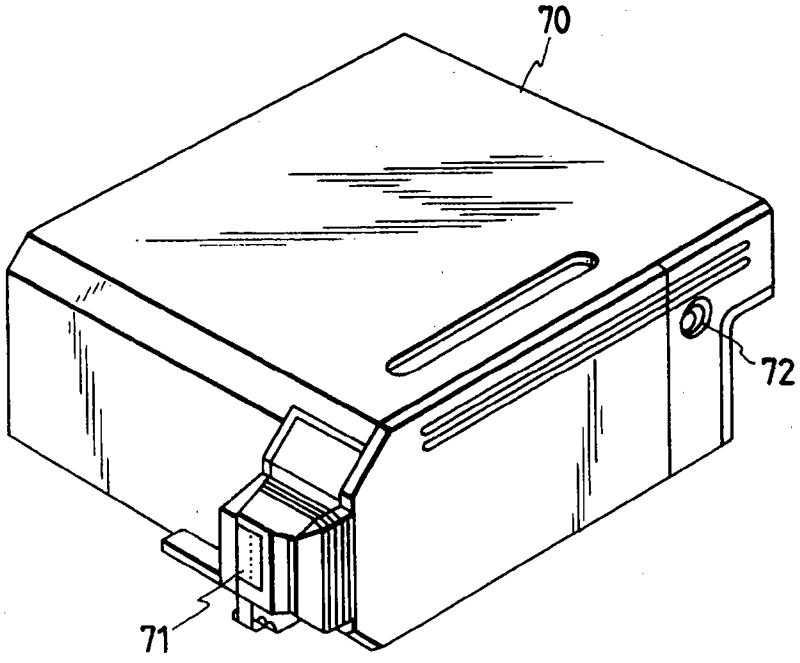


FIG. 9

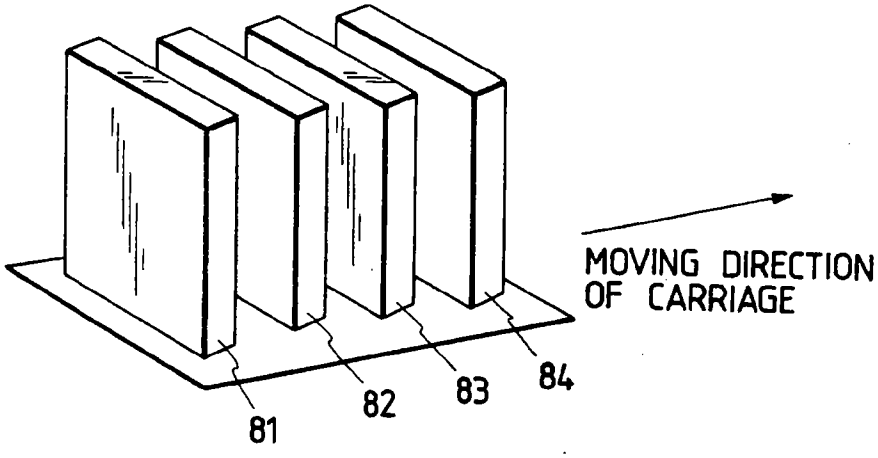
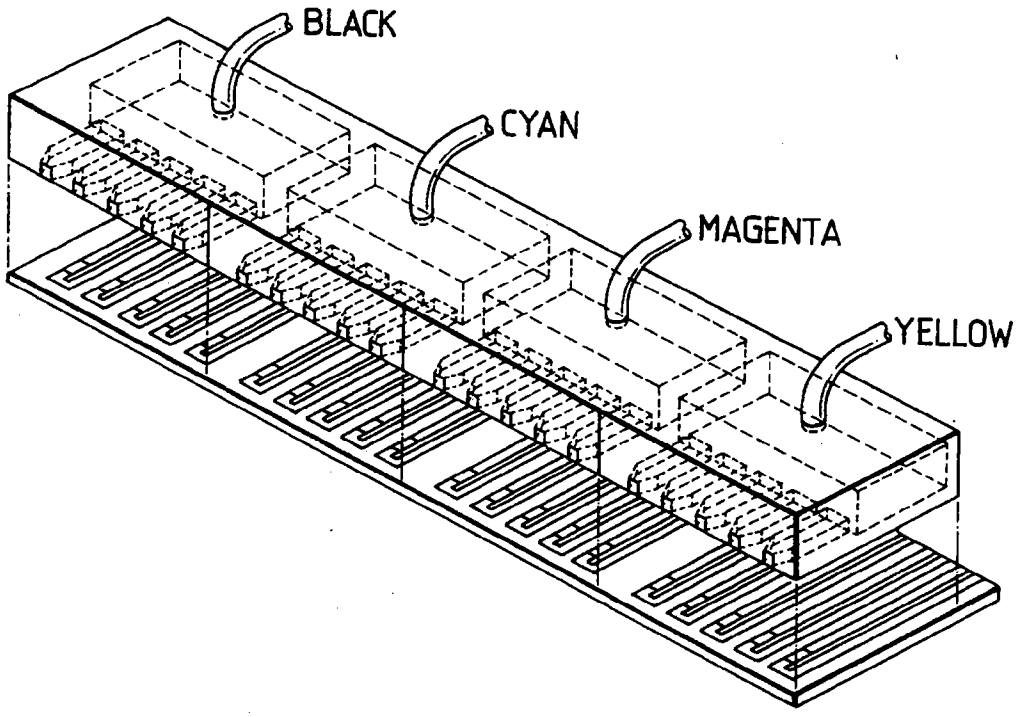

MOVING DIRECTION
OF CARRIAGE
81
82
83
84

FIG. 10


BLACK
CYAN
MAGENTA
YELLOW

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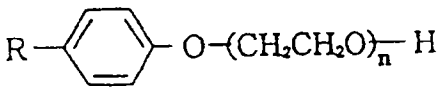
(54) Ink, ink-jet recording method, and ink-jet recording apparatus.

(57) Provided is an ink for ink-jet recording, comprising a dye, water, and the components (a), (b), and (c) below: (a) at least one surfactant selected from the group consisting of higher alcohol-ethylene oxide adducts represented by General Formula [1], alkylphenol-ethylene oxide adducts represented by General Formula [2], ethylene oxide-propylene oxide copolymers represented by General Formula [3], and acetylene glycol-ethylene oxide adducts represented by General Formula [4], at a content of from 0.1 to 20 % by weight;

$$R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}H \qquad [1]$$

where R is alkyl, and n is an integer;



[2]

where R is alkyl, and n is an integer;

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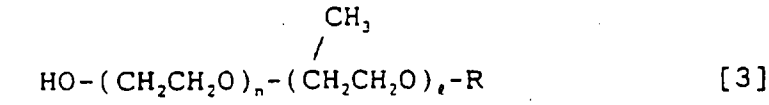
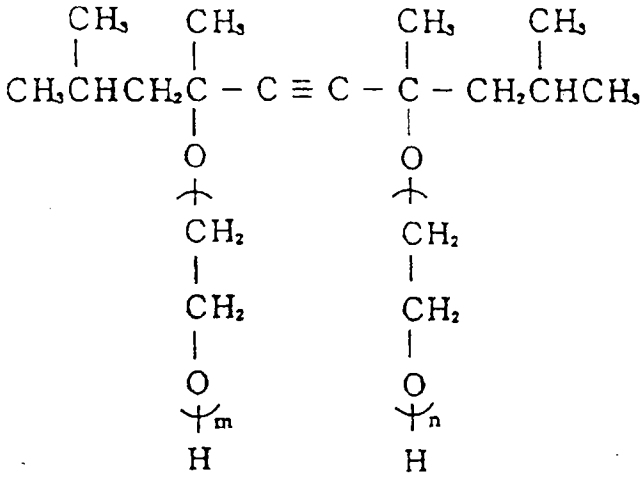


$$HO-(CH_2CH_2O)_n-(CH_2CH_2O)_{\ell}-R \qquad [3]$$

where R is alkyl, and n and ℓ are respectively an integer;



[4]

where m and n are respectively an integer;
(b) thiodiglycol; and
(c) urea or an derivative thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 0929

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	DATABASE WPI Week 8206, Derwent Publications Ltd., London, GB; AN 82-10725E & JP-A-56 167 775 (PILOT INK KK) 23 December 1981 * abstract *	1-11	C09D11/00
X	DATABASE WPI Week 8417, Derwent Publications Ltd., London, GB; AN 84-103558 & JP-A-59 045 372 (OGAWA KAKO KK) 12 March 1984 * abstract *	1-11	
A	DATABASE WPI Week 8246, Derwent Publications Ltd., London, GB; AN 82-98521E & JP-A-57 164 169 (RICOH KK) 8 October 1982 * abstract *	1-25	
A	GB-A-2 199 041 (CANON KABUSHIKI KAISHA) * examples 2-6 *	1-25	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C09D B41M
A	EP-A-0 447 896 (CANON KABUSHIKI KAISHA) * ink E * * abstract *	1-25	
A	US-A-5 116 409 (JOHN R. MOFFATT) * abstract * * column 3, line 48 - line 64 *	26,27,29	
A	EP-A-0 483 610 (HEWLETT-PACKARD COMP.) * claims 1,15 *	26,27,29	

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 July 1994	Girard, Y

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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T : theory or principle underlying the invention
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D : document cited in the application
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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 0929

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	EP-A-0 404 494 (XEROX CORP.) * page 3, line 25 - line 30; example 1 *	26,27	
A	EP-A-0 272 936 (CANON KABUSHIKI KAISHA) * page 4, line 19 - line 27; example 12 *	26	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)

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D : document cited in the application
L : document cited for other reasons

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The present European patent application comprised at the time of filing more than ten claims.

☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid,

namely claims:

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions.
namely:

see sheet -B-

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid.

namely claims:

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namely claims:

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☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

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The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

see sheet -B-

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namely claims:

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-25 : Ink composition for ink-jet recording comprising
   1) surfactant from a group of ethylene oxide adducts
   2) thiodiglycol
   3) urea or a derivative thereof

2. Claims 26-29: Colour ink-jet recording method and apparatus with ink containing non-ionic surfactant which is ejected in amounts of 10-70 pl; the feathering rate is 2.5 - 3.5